U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-290 515

Bench Scale Development of Meyers Process for Coal Desulfurization

TRW Systems Group, Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Jan 79

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

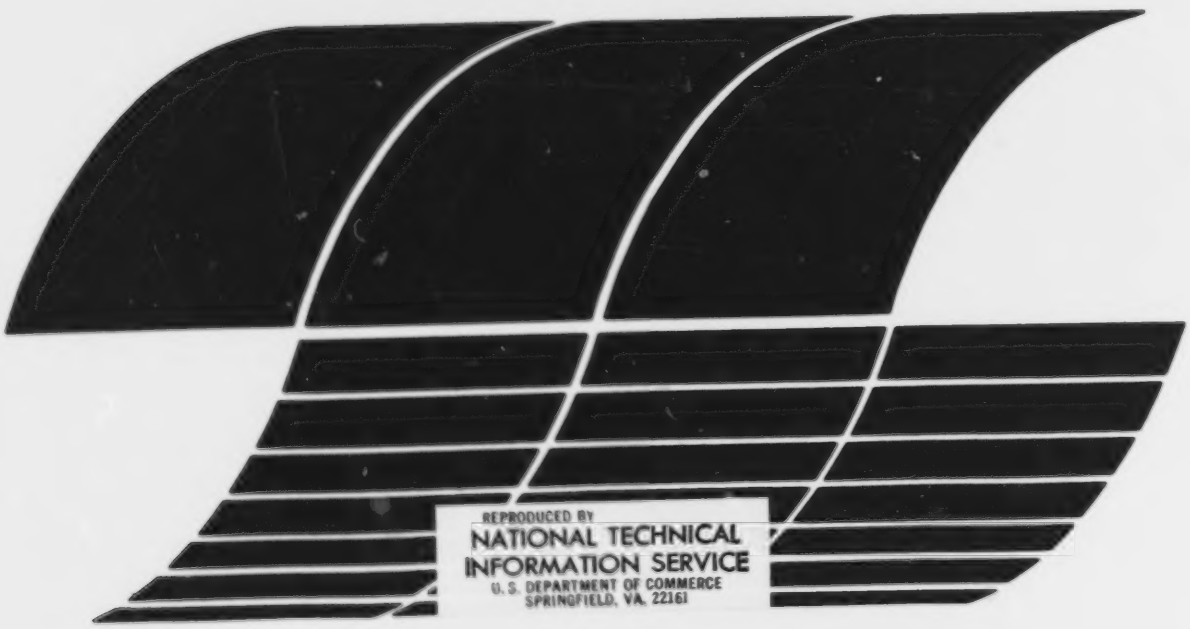
EPA-600/7-79-012
January 1979

PB 290515

EPA

Bench Scale Development of Meyers Process for Coal Desulfurization

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-012	2.	3. RECIPIENT'S ACCESSION NO. PB290315
4. TITLE AND SUBTITLE Bench Scale Development of Meyers Process for Coal Desulfurization		5. REPORT DATE January 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. A. Meyers, E. P. Koutsoukos, M. J. Santy, and R. Orsini		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS TRW Systems Group One Space Park Redondo Beach, California 90278		10. PROGRAM ELEMENT NO. EHB527 11. CONTRACT/GRANT NO. 68-02-2121
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 11/75 - 10/77 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Lewis D. Tamny, Mail Drop 61, 919/541-2709.

16. ABSTRACT The report gives results of coal desulfurization experiments to determine the feasibility and advantages of combining gravity separation of coal with chemical desulfurization. The investigations led to the definition of the Gravichem Process, a combination physical/chemical coal desulfurization scheme involving Meyers Process reagent and chemistry. Two coals were investigated: a run-of-the-mine coal sample and a mine-cleaned (MC) coal sample, both from the Martinka Mine, Lower Kittanning seam, and furnished by the American Electric and Power System (AEP Utility). Coal selection was influenced by the 60 million tons of recoverable Martinka Mine coal reserves, by the availability of coal output from a modern, commercial size, physical coal cleaning plant at the same mine, and by AEP's expressed interest in physical and chemical coal desulfurization as a means of solving sulfur pollution problems. MC Martinka coal will be the first coal to be tested at the 8 tons per day Meyers Process Reactor Test Unit.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Chemical Cleaning Coal Coal Preparation Desulfurization Gravity Separation	Pollution Control Stationary Sources Meyers Process Gravity Separation Gravichem Process	13B 13H 08G, 21D 08I 07A, 07D 20K

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	104
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE A06 - A01

EPA Form 2220-1 (9-73)

EPA-600/7-79-012

January 1979

Bench Scale Development of Meyers Process for Coal Desulfurization

by

R.A. Meyers, E.P. Koutsoukos,
M.J. Santy, and R. Orsini

TRW Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. 68-02-2121
Program Element No. EHB527

EPA Project Officer: Lewis D. Tamny

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ii

ABSTRACT

The report gives results of coal desulfurization experiments to determine the feasibility and advantages of combining gravity separation of coal with chemical desulfurization. The investigations led to the definition of the Gravichem Process, a combination physical/chemical coal desulfurization scheme involving Meyers Process reagent and chemistry. Two coals were investigated: a run-of-the-mine coal sample and a mine-cleaned (MC) coal sample, both from the Martinka Mine, Lower Kittanning seam, and furnished by the American Electric and Power System (AEP Utility). Coal selection was influenced by the 60 million tons of recoverable Martinka Mine coal reserves, by the availability of coal output from a modern, commercial size, physical coal cleaning plant at the same mine, and by AEP's expressed interest in physical and chemical coal desulfurization as a means of solving sulfur pollution problems. MC Martinka coal will be the first coal to be tested at the 8 tons per day Meyers Process Reactor Test Unit.

CONTENTS

Abstract ii
Figures iv
Tables v

1. Introduction 1
2. Bench-Scale Physical Chemical Desulfurization Data 3
   2.1 Coal processing procedures. 4
   2.2 Gravity separation results. 10
   2.3 Chemical leaching data. 15
      2.3.1 ROM Martinka coal processing results . . . 15
      2.3.2 Mine cleaned Martinka coal processing results. 24
3. Product Sulfur and Iron Recovery Investigations. 31
   3.1 Elemental sulfur recovery from pyrite leached coals 32
   3.2 Product sulfate and iron recovery 40
4. Process Engineering. 49
   4.1 Design basis. 50
   4.2 Conceptual process design for commercial scale. . . . 58
   4.3 Process steam balance 73
5. Process Cost Estimate. 77
   5.1 Equipment list. 77
   5.2 Capital and operating costs 83
6. Gravichem Treatment of Additional Coal Samples 85
   6.1 Gravichem treatment of TVA coal 85
   6.2 Gravichem treatment of Duquesne coal. 85

References. 90
Meyers Process Bibliography 91

Figures

Number		Page
1	Meyers Process Flow Diagram.	1
2	Gravichem Process.	2
3	Bench-Scale Gravity Separation - Chemical Desulfurization Processing Schemes	7
4	Pyritic Sulfur Leaching Data from MCM Coal Coal and Its Density Fractions	26
5	Sulfur and Iron Product Recovery Scheme.	33
6	Elemental Sulfur Recovery by Aqueous-Acetone Mixtures from Meyers Process Leached Coals	38
7	Recovery of Ferrous Sulfate by Evaporative Concentration of 5% w/w Iron Reagent Solutions	44
8	Chemical Cleaning of Coal with the Meyers Process.	51
9	TRW Coal Desulfurization Process Flow Sheets	59-61
10	TRW Coal Desulfurization Process Steam Balance	74
11	Gravichem Processing of TVA Coal	86
12	Photograph of Processed TVA Coal	88

TABLES

Number		Page
1	Gravity Separation Data on 3/8 x 0 ROM Martinka Coal.	11
2	Gravity Separation on 3/8 x 0 Top-Size Mine Cleaned Martinka Coal	11
3	Organic Liquid and Meyers Process Reagent Coal Separation at 1.3 Specific Gravity (3/8 Inch x 0)	12
4	Rate Data on Processing ROM Martinka Coal with 5% w/w Iron Solution (4% H_2SO_4) at 102°C and Atmospheric Pressure.	16
5	Rate Data on Processing 1.9 Sp. Gr. Martinka Coal Float Fraction with 5% Iron Solution (4% H_2SO_4) at 102°C and Atmospheric Pressure.	17
6	Rate Data on Processing 1.6 Sp. Gr. Martinka Float Fraction with 5% Iron Solution (4% w/w H_2SO_4) at 102°C and Atmospheric Pressure.	18
7	Rate Data on Processing 1.3 Sp. Gr. Martinka Coal Sink Fraction with 5% w/w Iron Solution (4% H_2SO_4) at 102°C and Atmospheric Pressure	19
8	Pyrite Removal Rate Constants for the ROM Martinka Coal as a Function of Gravity and Top-Size.	22
9	Pyrite Removal Rate Constants for Mine Cleaned Martinka Coal as a Function of Gravity Fraction and Top-Size.	25
10	Typical Desulfurization Data from Processing Mine Cleaned Martinka Coal and Selected Gravity Fractions Thereof	28
11	Gravichem Processed MCM Coal (14 x 0 Mesh).	30
12	Elemental Sulfur Recovery Data Using Aqueous Acetone Extractions	36
13	Multi-Stage Acetone Extractions of Elemental Sulfur from Processed Coal.	37

TABLES (continued)

Number		Page
14	Recovery of Ferrous Sulfate from Iron Sulfate H_2SO_4 Reagent by Evaporative Concentration.	43
15	Calcium Solubility Data in Iron Sulfate-Sulfuric Acid Solutions.	47
16	Process Mass Balance for Fine Coal (Stream Flows in Tons Per Hour)	62-67
17	Coal Desulfurization Process Equipment List	78-81
18	Leach Solution Gravity Separation Process Economics	84
19	Gravichem Processing of TVA Coal	87
20	Particle Size Distribution of Size-Reduced TVA Sink Coal . . .	87
21	Gravichem Processing of Duquesne Coal.	89

1. INTRODUCTION

The Environmental Protection Agency is sponsoring the development of a process for utilizing aqueous ferric sulfate to chemically and physically beneficiate coal. The chemical basis of the process involves the reaction of aqueous ferric sulfate with the pyritic sulfur content of coal to form about equal parts of sulfate and elemental sulfur. The sulfate dissolves into the iron sulfate leach solution and is subsequently limed-out to give a gypsum-iron oxide product. The generated elemental sulfur is extracted from the coal utilizing either an organic solvent or a drying procedure. This technique, termed the Meyers Process (Figure 1), has been demonstrated

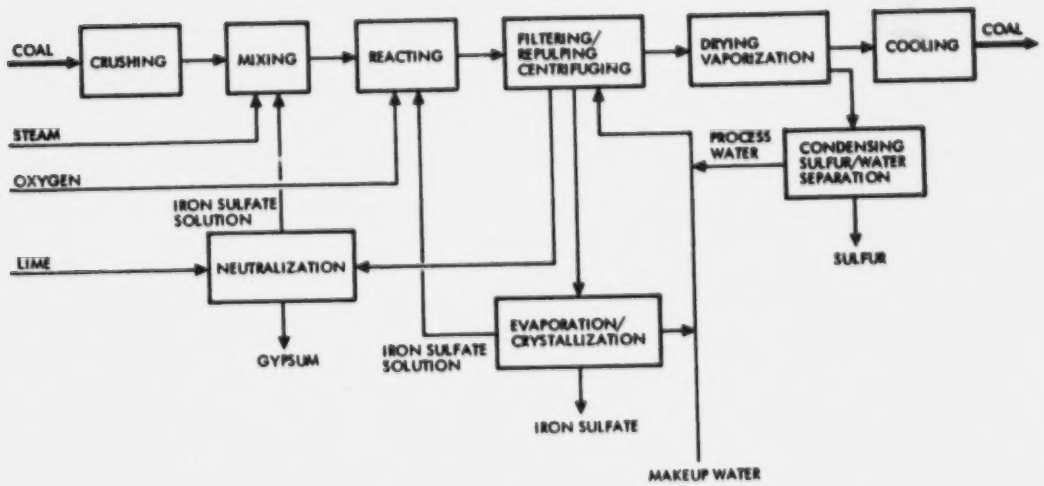


Figure 1. Meyers Process Flow Diagram

to remove 90-95% of the pyritic sulfur from U.S. coals in an EPA sponsored survey of 35 run-of-mine coals representative of United States coal. In

addition, more than 200 fully material balanced bench-scale experiments have been performed which have defined the process kinetics, material and energy balance. An up-to-date bibliography is presented in the Appendix.

In this program we have successfully demonstrated at bench scale that the Meyers Process iron sulfate leach solution, which has a specific gravity of 1.2-1.4, can be advantageously used to perform a preliminary float-sink separation of coal (Figure 2). This allows about one-half of the coal to bypass the process as a low-sulfur, high-heat content premium product which may be blended back with sink coal, desulfurized by the Meyers Process, or used to meet more stringent control requirements. This physical separation in combination with the Meyers Process is termed the "gravichem process".

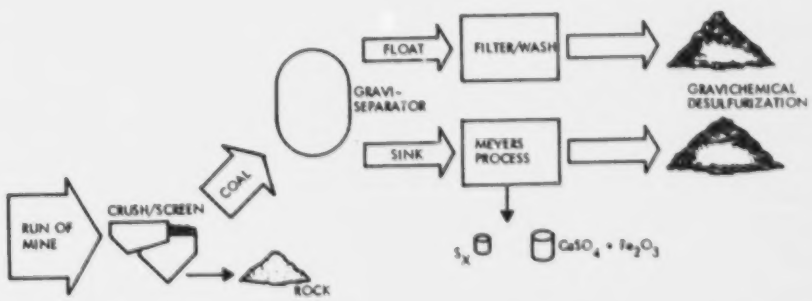


Figure 2. Gravichem Process

Because of the gravichem advance, which allows about one-half of the coal to bypass the reactor and sulfur extraction portions of the process, and other advances effected during this current project, the integrated (gravichem) Meyers Process forecast costs have been significantly reduced and are now calculated at \$85/KW capital cost and $\$0.35/10^6$ btu overall processing costs including plant amortization.

Data and data analysis for each process unit of the gravichem system are presented in the first two sections of this report. Process engineering and process cost estimations are next, followed by the results of a recent project add-on for evaluation of Tennessee Valley Authority and Duquesne Power and Light supplied coal samples.

2. BENCH SCALE PHYSICAL-CHEMICAL DESULFURIZATION DATA

Coal desulfurization experimentation conducted under this contract was directed principally at determining the feasibility and advantages of combining gravity separation of coal with chemical desulfurization. These investigations led to the definition of the gravichem process, a combination of physical-chemical coal desulfurization technology involving the Meyers Process reagent and chemistry.

Two coals were investigated: A Run-of-the-Mine (ROM) coal sample and a Mine Cleaned (MC) coal sample. Both samples were mined from the Martinka mine, Lower Kittanning seam, and were furnished to TRW by the American Electric and Power System (AEP Utility). Coal selection was influenced by the 60 million tons of recoverable Martinka mine coal reserves, by the availability of coal output from a modern, commercial size, physical coal cleaning plant at the same mine, and by AEP management's expressed interest in physical and chemical coal desulfurization as a means of controlling sulfur-oxide emissions to meet published emission standards. AEP supplied the coal samples for this program and promised to furnish additional samples for future testing including scale up testing. Coal selection was approved by the EPA Project Officer. Mine cleaned Martinka coal will be also the first coal to be tested at the eight tons per day Meyers Process Reactor Test Unit (RTU).

Samples from each of the two coals were gravity separated into sink and float fractions through the use of liquid media in the specific gravity range of 1.3 to 1.9. Organic liquids and Meyers Process reagent solutions were used to affect the separation. Heavy media separation, 1.9 specific gravity was aimed at the improvement of chemical desulfurization rates and at increasing the heating value of the coal by selective separation of low fuel value sink fraction (inorganic slate and slow to react, low surface-to-volume ratio pyrite particles with less than ten percent of the organic matrix associated with the inorganic reject). Separation at lower densities was aimed at the generation of a float fraction which met the NSPS for sulfur-oxide emissions

without chemical desulfurization or could meet the SO_x emission standards when combined with the Meyers Process depyritized sink fraction. Sections 2.1 through 2.3.2 detail the procedures used, the data obtained, and the conclusions drawn from such data.

2.1 COAL PROCESSING PROCEDURES

Coal processing experimentation consisted of gravity separation and of chemical leaching operations performed in sequence. The "as received" Martinka coals were size reduced, physically and chemically characterized, and then density separated and chemically depyritized at the desired processing conditions. The principal parameter investigated was flotation media density for its effect on ash and sulfur partitioning during separation and ash and sulfur leaching during chemical desulfurization. Additional parameters examined for their effect on pyrite leaching from gravity separated coal were coal top-size, temperature, oxygen partial pressure, acid concentration, and copper ion concentration.

The two Martinka coals used in this experimentation differ in two respects: time of acquisition and, therefore, location within the mine and preshipment processing at the mine. One of the coals, referred to here as the ROM Martinka sample, was mined from the coal seam substantially free of overburden and underlying rock in February 1976; approximately 220 pounds of this coal was shipped to TRW by AEP at a 6-inch top-size. The second coal represents the output of AEP's recently completed (1976) mine mouth physical cleaning plant. A 400-pound, 1-1/4 inch top-size sample of this coal was obtained for bench-scale experimentation from a 100-ton lot shipped to TRW in December 1976 for use in the shakedown of the Meyers Process RTU (EPA Contract No. 68-02-1880). The second coal is referred to as the "mine-cleaned Martinka", MCM, coal in this report.

Each of the "as received" coarse coal samples was crushed to 3/8-inch top-size, riffled, and sampled for characterization. Physical characterization consisted of particle size distribution determinations. Chemical characterization included short proximate (moisture, ash, heat and total content), sulfur forms (pyritic, sulfate, organic sulfur), and ash iron analyses.

These determinations were performed on multiple samples. Duplicate ultimate and trace element determinations were also performed on each of the two coals.

Gravity separations were performed on 3/8-inch top-size coal in the specific gravity range of 1.3 to 1.9 utilizing mixtures of toluene and perchloroethylene or perchloroethylene and ethylene bromide. Organic flotation media were used for coal separations at bench-scale because of flexibility in formulating the desired density and because of ease in handling. (Organic liquids are commercially used to simulate at bench-scale coal physical cleaning by iron suspensions practiced commercially.) Data generated in this program demonstrated that good agreement was also attainable between organic liquid separations and those obtained with Meyers Process reagent, aqueous iron sulfate-sulfuric acid solutions, at 1.3 specific gravity. Commercially, it is anticipated that the Meyers Process reagent will be used in cases where coal separation at specific gravities of about 1.3 or less is desirable. Gravity separations were carried out in batch mode. Coal samples to be float-sink separated were predried at 100°C under vacuum to ensure uniformity in feed coal moisture. The dry 3/8-inch top-size coal was size fractionated into 3/8-inch x 14 mesh and 14 mesh x 0 fractions which were cleaned separately employing the following steps: 1) thorough wetting of the coal with the appropriate media solution, 2) 30-60 minutes float-sink equilibration (settling), 3) isolation of the desired float or sink coal fraction, and 4) coal drying. Cleaned coal size fractions were recombined after drying and prior to further size reduction, riffling, and/or to chemical desulfurization. In 1.3 specific gravity separations with Meyers Process reagent the sink fraction in step 3 was retained as slurry for chemical leaching at the desired conditions; the sink slurry served as feed to the chemical depyritization reactor (Meyers Process). The float fraction was separated from the reagent by filtration, washed, dried, and analyzed. All float and sink fractions of any consequence were chemically characterized by short prox, sulfur forms, and ash iron analyses.

Preliminary gravity separation tests on ROM Martinka coal with 1.3, 1.4, 1.5, 1.6, 1.7 and 1.9 specific gravity liquids revealed that

float-sink separations at 1.3, 1.6 and 1.9 specific gravity values were best suited for investigating the effect of gravity separation on coal depyritization.

In general, the 1.9 and 1.6 float fractions and the 1.3 sink fraction were chemically leached subsequent to gravity separation. Figure 3 depicts two processing schemes used for bench-scale investigation of combined gravity separation-chemical desulfurization processing. In Scheme A the Meyers Process reagent was used for 1.3 specific gravity separation. In experiments where the same separation was performed with organic liquids the sink-slurry was processed by Scheme B in a manner analogous to that indicated for the 1.9 and 1.6 specific gravity float fractions. Chemical desulfurization processing (Meyers Process) beyond the "mixer" unit operation was the same for both schemes. Chemical desulfurization involved the following basic unit operations: mixer, reactor, coal-washing unit, elemental sulfur recovery unit, and drier. These operations were indicated in Figure 3 and are briefly described below. A wet or dry coal grinding step was included in Schemes A and B when coal separation and leaching were performed at different top-sizes.

In the "mixer" the ground coal, either whole coal or the separated float or sink fraction, was contacted with hot reagent and the resulting slurry brought to boiling under ambient pressure (103°C) in order to assure adequate coal wetting prior to transferring into the Meyers Process reactor. (In cases where the mixer was also used as the float-sink separator, the slurry was cooled to approximately 80°C to effect the separation prior to being transferred to Meyers Process reactor.) A degree of pyrite leaching occurred during the 30-60 minutes of mixer operation.

The bulk of pyrite leaching took place in the Meyers Process reactor. The reactor was operated either as a pryite leacher only, "ambient pressure reactor", or as a pyrite leacher-reagent regenerator, "L-R reactor", or as a two-stage reactor where most of the pyrite was oxidized under L-R conditions and the remaining under ambient pressure processing (topping reactor). Ambient pressure processing was conducted principally at 102°C,

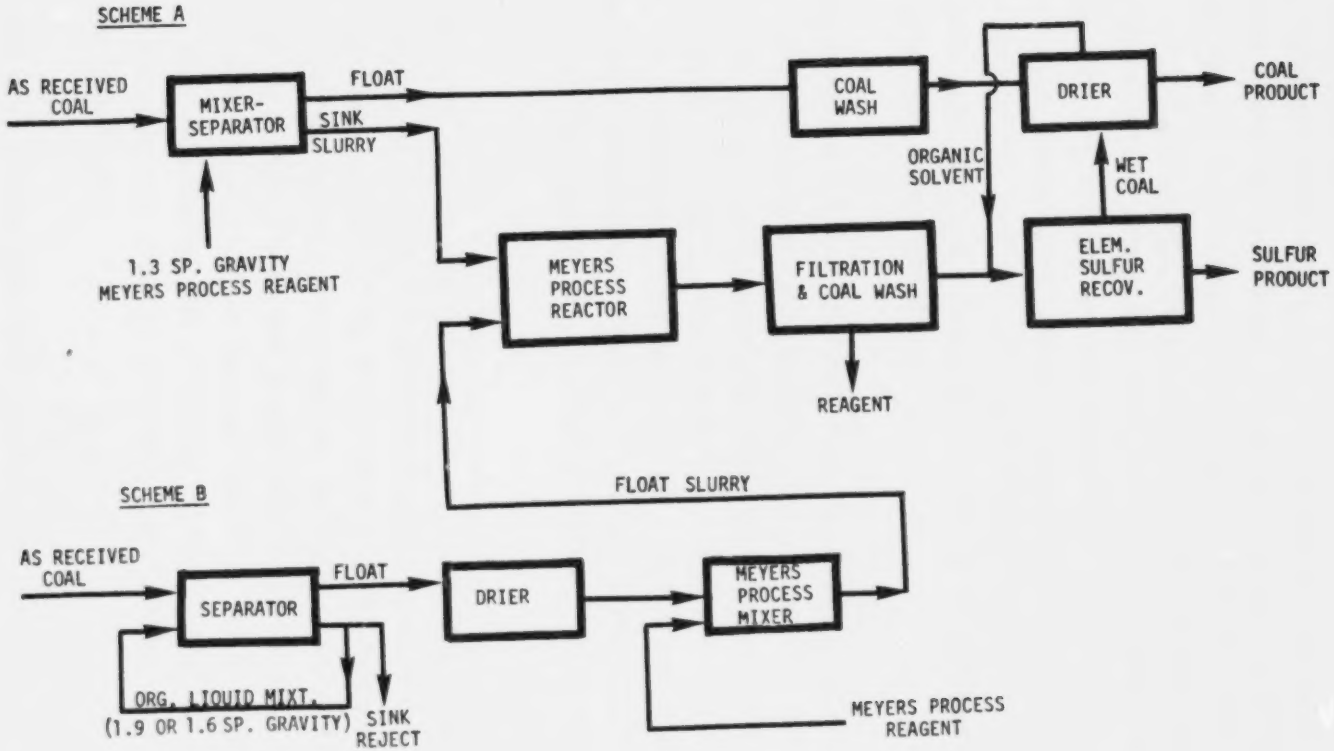


Figure 3. Bench-Scale Gravity Separation - Chemical Desulfurization Processing Schemes

the reflux temperature of the coal slurry prepared with acidified ferric sulfate containing nominally 5 wt. percent iron and 4 wt. percent sulfuric acid. Leaching residence time varied from 3 to 48 hours. Consumed ferric ion was replenished either by continuous or periodic reagent exchanges. Iron forms in the reagent solution were determined at frequent reaction time intervals. In L-R processing oxygen was fed to the leacher continuously for in-situ reagent regeneration; thus, there was no need for reagent exchange. The L-R reactor was operated in the 50 to 150 psig and 110°-130°C pressure and temperature ranges. Pressure operation of the L-R reactor was dictated by the need for efficient reagent regeneration. Slurry samples were taken every 0.5 hours during the first two hours of processing and every one hour thereafter.

Both ambient pressure and L-R reactors were operated as "well mixed" batch reactors. The ambient pressure reactors, including mixer and topping reactors were heated glass vessels equipped with mechanical stirrers. The L-R reactor was stirred by slurry circulation with the aid of a pump. The L-R reactor and its accessories (feed and sampling lines, pump, slurry circulation loop) were constructed, from 316 stainless steel stock. The approximate volume of the reactor was 13 liters; nominal slurry batch size was 8 liters.

Upon completion of the desired reaction time, the hot slurries from either the L-R reactor or the ambient pressure reactor were vacuum filtered. The reagent-wet coal was rinsed on the filter with a quantity of water equivalent to the estimated dry coal weight in the cake. The rinsed cake was then subjected to a slurry wash and a cake wash with two dry coal weights of water each. Slurry washes were performed at reflux temperature for 30 minutes. Iron analyses of the filtrates indicated that essentially complete reagent recovery was attained with this wash scheme. All filtrates were analyzed for iron forms.

The water-wet coal filter cake from the wash section was extracted with an organic solvent to recover the product elemental sulfur. Toluene was used in the majority of experiments until the more cost effective water-acetone system was developed under this program. Elemental sulfur recovery

from coal was virtually complete. The sulfur was recovered as a residue from the spent organic solvent. Each residue was analyzed for sulfur content.

The solvent wet coal was vacuum dried. The solvent was collected and weighed; the product coal was subjected to short proximate, sulfur forms, and iron analyses.

Product iron and sulfate were recovered either by crystallization of iron sulfate from spent reagent or by liming of spent reagent and/or spent wash water. Iron and sulfate recovery was utilized only in a limited number of experiments in order to define these sulfur product recovery techniques. Elemental sulfur recovery was performed in every experiment as a means of confirming pyrite leaching determined from before and after coal analyses and from ferrous ion production in ambient pressure processing. (In L-R processing ferrous ion is oxidized by the oxygen fed to the system and cannot be used as a measure of the quantity of pyrite leached from coal; total iron could be used but it is not an accurate measure of leached pyrite.)

Solids and liquid balances were performed for the complete process as well as for each of the unit operations (gravity separation, reactor, wash section, sulfur product recovery unit, drier). Iron and sulfur were also balanced in each experiment.

2.2 GRAVITY SEPARATION RESULTS

Tables 1 through 3 summarize gravity separation results obtained on two Martinka coals, ROM and Mine Cleaned, with two types of flotation media, organic liquids and Meyers Process reagent.

These data show that (a) substantial reduction in ash and inorganic sulfur can be attained with less than 4% loss in coal heat content by density separation at 1.9 specific gravity; (b) the 1.3 specific gravity float, representing 30-40% of the whole Martinka coal, meets the NSPS for sulfur-oxide emissions without chemical leaching and by the use of only a single stage separation; (c) the 1.3 gravity separation can be effected with Meyers Process reagent at least as efficiently as with organic liquids. These observations lead to the conclusion that substantial reduction in the costs of the chemical desulfurization of coal may be possible by effecting the 1.3 specific gravity separation in the Meyers Process "mixer" stage with the float bypassing the reactor. It may be also advantageous to physically clean the Meyers Process feed coal at 1.9 specific gravity whether the coal is separated at 1.3 specific gravity or not. This latter conclusion is strengthened by observed improvement in the leaching rate constant to be discussed in Section 2.3 of this report.

The data in Table 1 presents the principal findings from experimentation on the effect of gravity separation on Martinka ROM coal composition. It is noted that the 1.9 float fraction represents 90% of the weight of the ROM coal and approximately 96% of its heating value; however, its ash was reduced by 23%, its total sulfur content by 59% and its pyritic and sulfate sulfur forms by 72% and 50%, respectively. The simultaneous increase in heat content and decrease in sulfur content reduce substantially the amount of pyrite required to be leached chemically in order that the resulting coal meets the NSPS for sulfur-oxide emissions. In addition, only 90% of the coal needs to be leached chemically while the incurred heat value loss by discarding the sink fraction is less than 4%. Effects on leaching rate constant, which are also beneficial, are discussed in the next section.

TABLE 1. GRAVITY SEPARATION DATA ON 3/8-INCH x 0 ROM MARTINKA COAL

Coal Density Fraction	Fraction of Mine Cleaned Coal, (% w/w)	Coal Composition, % w/w (Except Heat Content), Dry						
		Ash	Heat Content, Btu/Lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron, Fe
Dry ROM Martinka Coal (Seam Sample)	100	18.12 ±0.09	12234 ± 16	3.62 ±0.09	2.81 ±0.06	0.22 ±0.03	0.59 ±0.02	3.18 ±0.08
1.9 Float (3/8" x 0)	90	13.91	13039	1.52	0.79	0.11	0.61	1.05
1.6 Float (3/8" x 0)	82	9.89	13685	1.23	0.53	0.08	0.63	0.65
1.3 Float (3/8" x 0)	41	3.97	14720	0.82	0.29	0.01	0.52	0.38
1.3 Sink (3/8" x 0)	59	26.59	10778	5.05	4.18	0.32	0.55	4.61

TABLE 2. GRAVITY SEPARATION ON 3/8-INCH TOP-SIZE MINE CLEANED MARTINKA COAL

Coal Density Fraction	Fraction of Mine Cleaned Coal, (% w/w)	Coal Composition, % w/w (Except Heat Content), Dry						
		Ash	Heat Content, Btu/lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron Fe
Dried As Received MCM Coal	100	17.82 ±0.63	12461 ± 71	1.62 ±0.08	1.13 ±0.10	0.01 ±0.01	0.48 ±0.08	1.27 ±0.08
1.9 Float (3/8" x 0)	93	15.65	12879	1.26	0.84	0.01	0.41	0.82
1.9 Sink (3/8" x 0)	7	49.97	6559	7.89	7.85	0.04	0.00	7.93
1.6 Float (3/8" x 0)	80	10.98	13510	0.95	0.40	0.00	0.55	0.45
1.6 Sink (3/8" x 0)	20	53.57	7903	3.76	3.67	0.02	0.07	3.78
1.3 Float (3/8" x 0)	32	7.73	14219	0.86	0.29	0.00	0.57	0.34
1.3 Sink (3/8" x 0)	68	20.35	11971	2.04	1.60	0.02	0.42	1.75

TABLE 3. ORGANIC LIQUID AND MEYERS PROCESS REAGENT COAL SEPARATION AT 1.3 SPECIFIC GRAVITY (3/8 INCH x 0)

Flotation Medium	Coal Fraction (% w/w)	Ash (% w/w)	Heat Content (Btu/lb)	Total Sulfur, (% w/w)	Pyritic Sulfur, (% w/w)	Sulfate Sulfur, (% w/w)	Organic Sulfur, (% w/w)	Iron (% w/w)	Lbs S/ MM Btu
Organic Liquid									
(Float)	30	2.64	14711	0.74	0.06	0.01	0.67	0.15	0.50
(Sink)	70	17.34	12041	1.86	1.44	0.04	0.38	1.54	1.54
Meyers Process Reagent Soln.*									
(Float)	31	3.02	15057	0.80	0.06	0.01	0.73	0.20	0.53
(Sink)	69	14.97	12917	1.43	0.75	0.02	0.66	1.63	1.10

*Meyers Process Solution was 1.3 specific gravity Meyers Process leach solution containing 7.5% w/w Fe as $Fe_2(SO_4)_3$ and 4% w/w H_2SO_4.

The observations made on the 1.9 density separation of 3/8 inch top-size ROM coal are slightly more pronounced at 1.6 specific gravity. In this case the heat value loss, if the 18% sink is rejected, exceeds 8%. This penalty may outweigh the benefit of additional sulfur removal between 1.9 and 1.6 specific gravity separations.

Separation of ROM coal at 1.3 specific gravity appears to offer the most important processing advantage since by a single physical separation step up to 41% of the coal meets the NSPS for sulfur-oxide emissions (0.6 lbs sulfur/MM btu) without chemical desulfurization. As indicated in Table 1, the 1.3 float fraction has 14,720 btu/lb heat content and 0.82% w/w sulfur content or 0.56 lbs sulfur per million btu which is well under the standard. The sink fraction should meet the sulfur standard by chemical leaching after grinding to a finer top-size; however, pyritic and sulfate sulfur leaching from the sink fraction in excess of 95% would be required so that the recombined coal meets the NSPS. A more attractive approach would probably be to either float-sink the 1.3 sink fraction at 1.9 and reject the 1.9 sink with negligible heat value loss or to gravity separate at 1.3 the 1.9 float fraction of the ROM coal (Table 1, second row). The resulting sink fraction will have similar composition to that presented in the last row of data in Table 2. In this case 80%-85% chemical leaching of pyrite from the sink fraction would be sufficient to meet the NSPS for sulfur.

Table 2 presents data on gravity separation of MCM (mine-cleaned-Martinka) coal at 3/8-inch top-size. This coal was physically cleaned at a mine mouth commercial plant at 4-inch top-size and at approximately 1.6 specific gravity. As the data in Table 2 show, size reduction of the commercially cleaned coal leads to additional ash and pyrite rejection at 1.9 and 1.6 float-sink separations. The data in Table 2 indicates that it may be desirable to physically clean ROM coal at 3/8-inch top-size rather than at 4 inches; this conclusion is tentative since float-sink separation data attained by commercial processing of 3/8-inch top-size coal are not available. The data strongly suggest that it would be desirable to gravity separate ROM coal at 1.3 specific gravity after it has been scalped (light physical cleaning) to reduce its ash and free pyrite; the resulting 1.3

sink fraction would be expected to require shorter chemical processing to meet NSPS for sulfur-oxide emissions. It is noted that the 1.3 float fraction, which represented 32% of the MCM coal, met the 0.6 lbs sulfur per million btu emission standard without chemical leaching.

Comparison of the coal analysis data in Tables 1 and 2 shows that the float coals generated at a given specific gravity have nearly identical composition regardless of the ash and inorganic content of the whole coal, provided the latter is derived from the same mine.

The data in Table 3 illustrate the effect of flotation media on 1.3 specific gravity float-sink separated coal fractions. Organic liquids are compared with Meyers Process reagent solution. Again, there is no effect on float composition and again, both float coals meet the NSPS for sulfur-oxide emissions without chemical leaching. However, the sink composition data indicates that there is appreciable advantage to the use of Meyers Process reagent solution over organic liquids. The leach solution separated sink fraction contains half the pyritic sulfur of the sink fraction separated in organic liquid media; also, the total sulfur values of the sink fractions differ substantially whether they are compared on percent basis (Table 3, fifth column) or on per million btu basis (last column). The apparent negligible effect on the float fractions is due to the very low pyrite content of the 1.3 float.

The extent of pyrite leaching during gravity separation by Meyers Process reagent is exaggerated by the data in Table 3 since the separation was unnecessarily lengthy in this experiment (approximately 3 hours). However, regardless of the extent of pyrite removal in the separation step there are obvious processing advantages in utilizing the same reagent for coal separation and for coal leaching where appropriate. The combined separation-leaching technique by Meyers Process reagent has been labeled "gravichem processing".

2.3 CHEMICAL LEACHING DATA

Experimentation on density separation of coal was performed to generate the data on partitioning of ash and sulfur presented in the previous section but also to generate the appropriate samples in order to investigate the effect of density separation on rates of the chemical leaching of pyrite from coal. Pyrite leaching was performed on float-sink fractions of both ROM and mine cleaned (MC) Martinka coals. The whole coal was also leached in each case.

2.3.1 ROM Martinka Coal Processing Results

ROM Martinka coal and samples of the 1.9 and 1.6 specific gravity float fractions and the 1.3 specific gravity sink fraction were processed under atmospheric pressure at 102°C with ferric sulfate solution containing 5% w/w Fe and 4% w/w H_2SO_4. These coals were processed at both 3/8-inch and 14 mesh top-sizes for intervals up to 48 hours. Typical data from this experimentation (Experiment Nos. 1 through 23) are presented in Tables 4 through 7.

Data presented in Table 4 indicate that ambient pressure Meyers processing of ROM Martinka coal can effect at least 86% S_p removal at 14 mesh top-size and 73% S_p removal at 3/8-inch top-size in 24 and 48 hours, respectively, at 102°C. Also, the sulfate content of the feed coal was reduced by at least 50% at all reaction times used. It is noted, however, that prolonged processing (in excess of 24 hours) renders sulfate washing from coal more difficult. This is most likely due to increased permeation of the coal matrix by the leach solution which then necessitates longer wash contact times to enable complete diffusion of reagent from the coal. The data in Tables 4 to 7 appear to indicate that this phenomenon is more pronounced with the higher ash samples (whole ROM coal and 1.3 sp. gr. ROM sink fraction). This is another reason that light physical cleaning (e.g., 1.9 sp. gr. separation) of ROM coal prior to chemical leaching may be desirable.

The desirability of physical cleaning prior to chemical leaching is clearly illustrated by the data in Tables 5 and 6. These data demonstrate

TABLE 4. RATE DATA ON PROCESSING ROM MARTINKA COAL WITH 5% w/w IRON SOLUTION (4% H_2SO_4) AT 102°C AND ATMOSPHERIC PRESSURE

EXP NO.	Process Time, Hours	Coal Composition 5% w/w (Except Heat Content), Dry							% S_p Removal
		Ash	Heat Content Btu/lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron	
Starting Coal		18.12 ±0.09	12234 ± 16	3.62 ±0.09	2.81 ±0.06	0.22 ±0.03	0.59 ±0.02	3.18 ±0.08	
Processed at 14 Mesh Top-Size									
1	3	15.79	12847	2.07	1.49	0.00	0.58	1.57	47
2	5	15.99	12841	1.78	1.13	0.00	0.65	1.20	60
3	24	14.21	13013	1.18	0.39	0.11	0.68	0.39	86
Processed at 3/8-Inch Top Size									
4	3	17.42	12402	2.81	2.22	0.01	0.58	2.25	21
5	24	15.26	12911	1.83	1.20	0.00	0.63	1.38	57
6	48	13.67	13115	1.53	0.76	0.09	0.63	0.87	73

TABLE 5. RATE DATA ON PROCESSING 1.9 SP. GR. MARTINKA COAL FLOAT FRACTION WITH 5% IRON SOLUTION (4% H_2SO_4) AT 102°C AND ATMOSPHERIC PRESSURE

EXP. NO.	Process Time, Hours	Coal Composition 5% w/w (Except Heat Content), Dry							% S_p Removal
		Ash	Heat Content Btu/lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron Fe	
Starting Coal (1.9 Float)		13.91	13039	1.52	0.79	0.11	0.61	1.05	
Processed at 14 Mesh Top-Size									
7	3	11.76	13416	1.08	0.36	0.11	0.61	0.61	54
8	24	12.05	13355	0.80	0.16	0.01	0.63	0.34	80
Processed at 3/8-Inch Top-Size									
9	3	12.97	13291	1.17	0.69	0.00	0.48	0.77	10
10	5	12.92	13217	1.13	0.57	0.01	0.55	0.66	26
11	24	12.23	13410	0.96	0.23	0.06	0.67	0.44	70
12	48	11.19	13371	1.04	0.31 ?	0.13	0.60	0.56	60 ?

TABLE 6. RATE DATA ON PROCESSING 1.6 SP. GR. MARTINKA FLOAT FRACTION WITH 5% IRON SOLUTION (4% w/w H_2SO_4) AT 102°C AND ATMOSPHERIC PRESSURE

EXP NO.	Process Time, Hours	Coal Composition 5% w/w (Except Heat Content), Dry							% S_p Removal
		Ash	Heat Content But/lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron Fe	
Starting Coal (1.6 Float)		9.89 ±0.06	13685 ± 45	1.23 ±0.07	0.53 ±0.03	0.08 ±0.01	0.63 ±0.04	0.65 ±0.06	
Processed at 14 Mesh Top-Size									
13	3	8.99	13929	0.84	0.29	0.00	0.55	0.35	45
14	24	8.57	13908	0.68	0.11	0.02	0.55	0.26	79
Processed at 3/8-Inch Top-Size									
15	3	10.18	13676	1.01	0.44	0.00	0.57	0.49	17
16	24	9.01	13935	0.96	0.19	0.03	0.74	0.34	64
17	48	8.97	13922	0.91	0.21	0.03	0.67	0.35	60

TABLE 7. RATE DATA ON PROCESSING 1.3 SP. GR. MARTINKA COAL SINK FRACTION WITH 5% w/w IRON SOLUTION (4% H_2SO_4) AT 102°C AND ATMOSPHERIC PRESSURE

EXP. NO.	Process Time, Hours	Coal Composition 5% w/w (Except Heat Content), Dry							% S_p Removal
		Ash	Heat Content Btu/lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron Fe	
Starting Coal (1.3 Sink)		26.59	10778	5.05	4.18	0.32	0.55	4.61	
Processed at 14 Mesh Top-Size									
18	3	26.34	11089	3.48	3.00	0.07	0.41	3.21	28
19	24	22.56	11659	1.75	1.08	0.15	0.52	1.42	74
20	48	22.28	11604	1.62	0.82	0.18	0.62	1.31	80
Processed at 3/8-Inch Top-Size									
21	3	25.40	11185	3.89	3.49	0.04	0.36	3.69	17
22	24	23.61	11379	2.79	2.24	0.12	0.43	2.29	46
23	48	22.95	11554	2.13	1.43	0.13	0.57	1.80	66

that the NSPS for sulfur-oxide emissions can be met by processing the 14 mesh top-size 1.9 and 1.6 specific gravity float fractions of the Martinka coal for 24 hours or less at 102°C. Neither the whole ROM coal nor the 1.3 sink fraction (Table 7) met the above standard or even approached it in 24 hours. It should be noted, however, that high pyritic sulfur removal (80% and 74%, respectively) was attained with both these coals after 24 hours of 102°C processing.

The sulfur-oxide emission standard was also approached with the 3/8 inch top-size float fractions after 24 hours of processing but further reaction time did not change the residual pyrite beyond normal uncertainties in sulfur form analyses (Tables 5 and 6); in fact, in both cases (Experiment Nos. 12 and 17) a slight pyritic sulfur increase was registered attributed to normal size errors in analyses. Residual S_p values of both gravity fractions at both top-sizes were reduced to approximately 0.20 or less after 24 hours processing.

In order to assess the observed impact of physical cleaning on the chemical desulfurization of Martinka coal, the rate data generated in this investigation were correlated with the end of the empirical pyrite leaching rate expression presented below (Equation 1). This rate expression was formulated from extensive leaching data on high sulfur Lower Kittanning coal generated during earlier bench-scale investigations.

$$r_L = - \frac{dWp}{dt} = K_L W_p^2 Y^2 \qquad (1)$$

where

r_L Is the pyrite leaching rate, expressed in weight of pyrite removed per 100 weights of coal per hour (rate of coal pyrite conc. reduction),

W_p Is the pyrite concentration in coal at time t, in wt. percent,

t Is the reaction (leaching) time, in hours,

Y Is the ferric ion-to-total iron ratio in the leacher at time t, dimensionless, and

K_L Is the pyrite leaching rate constant (a function of temperature and coal particle size), expressed in $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$.

with

$$K_L = A_L \exp(-E_L/RT) \qquad (2)$$

where

A_L Arrhenius frequency factor, in the units of K_L,

E_L Apparent activation energy, in calories/mole,

R Gas constant, in calories/mole/°K, and

T Absolute temperature, in °K.

Using Equation 1 and measured (analyzed) W_p and Y values versus reaction time at 102°C, pyrite reaction rate constants, K_L, were computed for ROM Martinka coal and its 1.9 and 1.6 specific gravity float fractions and 1.3 specific gravity sink fraction at 14 mesh and 3/8 top-size. The computed K_L values are presented in Table 8. The standard deviations indicated in Table 8 represent the uncertainty in K_L introduced by scatter in sulfur forms analyses. As would be expected, the absolute uncertainty in K_L tends to increase as S_p° (starting pyritic sulfur value) decreases. Hence, the greatest absolute uncertainty resides with K_L values computed for the 1.6 specific gravity float fraction.

The activation energy, E_L, was previously estimated to be 11.1 Kcal/mole and is considered to be specific to the pyrite leach reaction and independent of coal density fraction or top-size. Using this E_L value and the rate data generated at 102°C, pyrite leaching as a function of time or reactor size can be predicted for any of the coals listed in Table 8 at any temperature range that Equation 2 is valid and A_L and E_L remain constant. Strictly speaking, however, these reactor design data are only valid for well mixed reactors.

TABLE 8. PYRITE REMOVAL RATE CONSTANTS FOR THE ROM MARTINKA COAL AS A FUNCTION OF GRAVITY FRACTION AND TOP-SIZE

Coal Gravity Fraction	Reaction Rate Constant, K_L, $W_p^{-1}hr^{-1}$ at 102°C	
	14 Mesh Top-Size	3/8-Inch Top-Size
ROM (Whole Coal)	0.08 ± 0.011	0.02 ± 0.001
1.9 Sp. Gr. Float	0.24 ± 0.095	0.08 ± 0.035
1.6 Sp. Gr. Float	0.42 ± 0.198	0.09 ± 0.064
1.3 Sp. Gr. Sink	0.03 ± 0.017	0.01 ± 0.003

The data in Table 8 verify expectations that pyrite removal rate constant enhancement can be achieved through physical coal cleaning. Light physical cleaning (1.9 sp. gr.) is seen to increase the reaction rate constant by a factor of 3-4 for 14 mesh and 3/8-inch top-size coals. Deeper cleaning at 1.6 specific gravity further reduces the S_p content of the coal and may additionally increase the rate constant by as much as a factor of 2. This K_L enhancement may be attributed to removal by physical cleaning of slow reacting pyrite particles which have low specific surface area or which are isolated by the organic matrix and have low reagent accessibility. Under this assumption one would expect clean coal sink fractions to react with a rate constant which is lower than that of the ROM coal. In fact, this is what is observed with the 1.3 specific gravity sink fraction. This pyrite and ash enriched fraction was found to react with a K_L value which is less than half that of the ROM coal.

An alternate interpretation of the decrease in rate constant of the 1.3 sink fraction may be attributed to the empirical nature of the reaction rate expression employed. Consider an integrated form of the reaction rate expression Equation (3):

$$t = \frac{\frac{1}{W_p} - \frac{1}{W_p^\circ}}{K_L \bar{Y}^2} \qquad (3)$$

where

t - Is the time required to reduce coal pyrite to Wp, in hours,

W_p° - Is the pyrite concentration of the starting coal, in wt. percent, and

$\bar{Y}$ - Is the average ferric ion-to-total iron ratio during reaction, dimensionless.

In the case of 50% pyrite removal this expression reduces to:

$$t = \frac{1}{W_p^\circ K_L \bar{Y}^2}$$

Consider now a fixed quantity of ROM Martinka coal which requires a period of processing time, t, under specified conditions to achieve 50% S_p removal. If a portion of the pyrite-free organic matrix were to be removed from this coal sample prior to reaction, the value of W_p° would, of course, increase. Yet, since the absolute quantity of pyrite in the sample is unchanged, the time required to achieve 50% removal will remain unchanged; namely, t (assuming that there is no matrix effect upon reaction rate). Since t is inversely proportional to the product of W_p° and K_L, the apparent value of K_L must decrease when the value of W_p° is artificially increased as described. This situation is analogous to that encountered during the 1.3 specific gravity cleaning since the 1.3 specific gravity float fraction is essentially pyrite free. Thus, owing to the empirical nature of the employed reaction rate equation, the rate constant, K_L, of a given coal can be artificially manipulated through the addition or removal of pyrite-free material. An identical numerical treatment may be applied to the 1.9 and 1.6 specific gravity float fractions if the assumption is made that pyrite particles are uniform with respect to specific surface area and are completely accessible to reagent; such treatment indicates that apparent rate constant enhancement on the order of that obtained experimentally would be expected.

Whether the observed rate constant enhancement through physical cleaning is partially or entirely due to the empirical nature of the rate expression is actually of academic importance only. Rate constant enhancement is, in any case, a measure of the reduction in process time required to attain a specified S_p content. The point of practical importance which was demonstrated through this study is that light physical cleaning is useful when used in conjunction with chemical desulfurization because it reduces Meyers Process plant requirements by 1) reducing the ash material to be processed and 2) reducing the processing time required to desulfurize ROM coal to meet the NSPS for sulfur-oxide emissions. Secondly, physical deep cleaning alone, while producing a float fraction which meets sulfur-oxide NSPS, yields a sink fraction containing more ash and slow reacting pyrite than is desirable as feed to a Meyers Process desulfurization unit. Thus, the use of light cleaning to remove rock and pyrite (at a minimum heat value loss) prior to coal separation appears to be highly desirable.

2.3.2 Mine Cleaned Martinka Coal Processing Results

The data presented in the previous section indicated that light physical cleaning of 3/8-inch top-size coal performed at bench-scale had a beneficial effect on subsequent chemical desulfurization. Investigations performed on this coal were aimed at examining the validity of the above observation when applied to a commercially cleaned coal at a much coarser size (4 inches versus 3/8-inch top-size). There was an added incentive to study this particular coal since it will be the first coal to be processed in the Meyers Process Reactor Test Unit.

The MCM coal and its 1.9 specific gravity float and the 1.3 sink fraction of such float (labeled 1.9 float-1.3 sink) were processed at 3/8-inch, 14 mesh and 100 mesh top-sizes. The process data from these coals indicated that the previously determined pyrite leaching rate expression (Equations 1 and 2) was applicable to them within the temperature range of this investigation, namely 95°C to 120°C. Furthermore, within the accuracy of the obtained analyses, the rate expression was found to be valid to at least 90% S_p removal. The 102°C leaching rate constants, K_L, computed from the process data are listed in Table 9. Comparison of mine cleaned K_L with

that of the 1.9 float fraction indicates that, as observed previously, cleaning has effected an increase in the pyrite removal rate constant.

TABLE 9. PYRITE REMOVAL RATE CONSTANTS FOR MINE CLEANED MARTINKA COAL AS A FUNCTION OF GRAVITY FRACTION AND TOP-SIZE

Gravity Fraction	K_L (102°C), W_p^{-1} hr^{-1}		
	3/8 Inch x 0	14 Mesh x 0	100 Mesh x 0
Mine Cleaned		0.10	0.25
1.9 Float		0.17	
1.9 Float-1.3 sink	0.02	0.13	

A summary of pyrite leaching rate data is presented in Figure 4. The solid curves represent pyritic sulfur decay in 14 and 100 mesh top-size MCM coal as a function of reaction time at 102°C based on Equations 1 and 2 and on the indicated K_L values. The data points represent pyritic sulfur analyses of coal processed for the indicated time at 102°C. Process times at temperatures other than 102°C were normalized to 102°C equivalent time by the use of the previously derived E_L value of 11.1 kilocalories per mole. The dashed curves represent the pyritic sulfur leaching rates from the 1.9 float and the 1.9 float-1.3 sink fractions of the MCM coal using the experimentally derived K_L values for these fractions listed in Table 9.

The data in Figure 4 indicate that the pyritic sulfur concentration of any of these coals dropped below 0.2% w/w in less than 30 hours of equivalent 102°C processing time. If product sulfur recovery is complete, most of these coals should meet or very nearly meet the NSPS for sulfur-oxide emissions after 30 hours of processing, since their organic sulfur content is less than 0.6% w/w (in most cases) and their heat content above

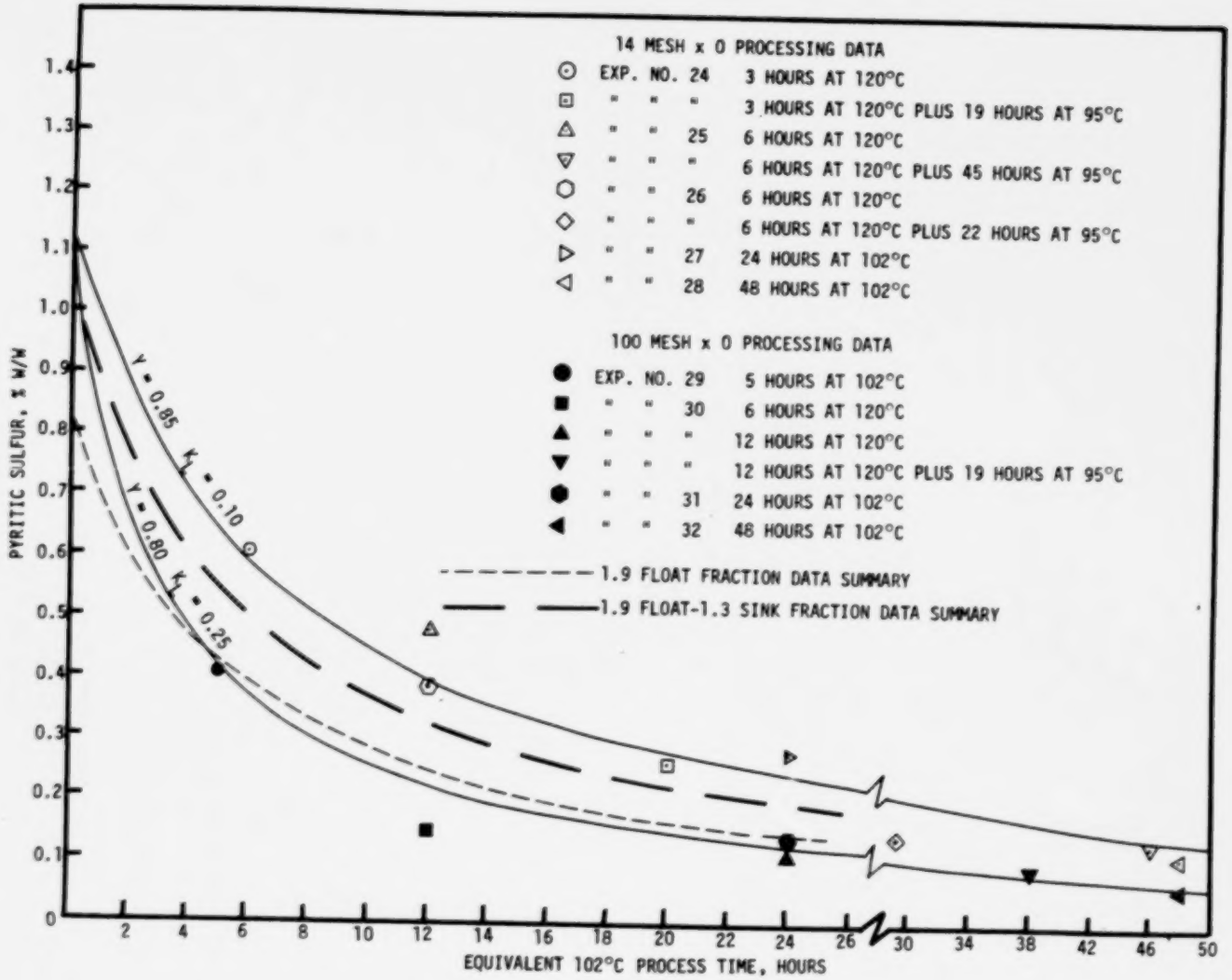

14 MESH x 0 PROCESSING DATA
EXP. NO. 24 3 HOURS AT 120°C
" " " 3 HOURS AT 120°C PLUS 19 HOURS AT 95°C
" " 25 6 HOURS AT 120°C
" " " 6 HOURS AT 120°C PLUS 45 HOURS AT 95°C
" " 26 6 HOURS AT 120°C
" " " 6 HOURS AT 120°C PLUS 22 HOURS AT 95°C
" " 27 24 HOURS AT 102°C
" " 28 48 HOURS AT 102°C
100 MESH x 0 PROCESSING DATA
EXP. NO. 29 5 HOURS AT 102°C
" " 30 6 HOURS AT 120°C
" " " 12 HOURS AT 120°C
" " " 12 HOURS AT 120°C PLUS 19 HOURS AT 95°C
" " 31 24 HOURS AT 102°C
" " 32 48 HOURS AT 102°C
1.9 FLOAT FRACTION DATA SUMMARY
1.9 FLOAT-1.3 SINK FRACTION DATA SUMMARY
Y = 0.85 K1 = 0.10
Y = 0.80 K1 = 0.25
PYRITIC SULFUR, % W/W
EQUIVALENT 102°C PROCESS TIME, HOURS

Figure 4. Pyritic Sulfur Leaching Data from MCM Coal and Its Density Fractions

12,500 btu per pound. Table 10 presents typical processed coal composition data for each of the four coals depicted in Figure 4. In each case the processed coal either met or approached the sulfur-oxide emission standard after approximately 24 hours of equivalent 102°C leaching time.

The K_L values in Table 9 and the data in Figure 4 show that mine cleaned coal reacted more slowly than would be expected of a cleaned coal. The previously studied ROM coal and its 1.6 float fraction (Section 2.3.1) reacted with rate constants of 0.08 and 0.42 W_p^{-1} hr^{-1}, respectively, at 14 mesh top-size. Hence, the mine cleaned sample reacted with a rate constant which is only 25% higher than that of the ROM coal and only one-fourth the rate constant of the laboratory prepared 1.6 float fraction. This result would be expected in view of the float-sink data presented in Table 2, Section 2.2, which revealed that the MCM contained approximately 20% of releasable 1.6 specific gravity sink material when size reduced from 4 inches to 3/8-inch top-size. This difference in rate constants between MCM (commercially cleaned at approximately 1.6 sp. gr.) and the laboratory prepared 1.6 float fraction from Martinka ROM coal is believed to be due entirely to the difference in coal top-size during cleaning. According to the Table 2 data the pyrite from the MCM coal should leach with a rate constant whose value lies between that of the ROM and the 1.9 specific gravity float. Comparison of the data in Tables 8 and 9 reveals this to be the case.

Experimentation performed with the ROM coal gravity fractions indicated that the 1.3 sink fraction was subject to a substantial decrease in rate constant from that of the ROM coal. This was thought to be attributable to segregation of slow reacting pyrite. This effect was found to be counteractable to some extent by removal of the 1.9 sink fraction. Thus, the 1.9 float-1.3 sink fraction rather than the whole 1.3 sink fraction was used predominately in the rate studies with MCM coal. As previously mentioned the 1.3 float fraction required no further processing to meet NSPS for sulfur-oxide emissions. Data presented in Table 9 verify the attractiveness of this approach; the 1.9 float-1.3 sink fraction reacted with 30% higher rate constants than did the mined cleaned coal. However,

TABLE 10. TYPICAL DESULFURIZATION DATA FROM PROCESSING MINE CLEANED MARTINKA COAL AND SELECTED GRAVITY FRACTIONS THEREOF

EXP NO.	Processing Conditions*	Top-Size, Mesh	Coal Composition % w/w (Except Heat Content)							S_p Removal
			Ash	Heat Content, Btu/Lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Coal Iron, Fe	
	Mine Cleaned Coal (5 Sample Average)		17.82 ±0.63	12481 ± 71	1.62 ±0.08	1.13 ±0.19	0.01 ±0.01	0.48 ±0.18	1.27 ±0.08	
26	6 Hrs 120°C + 22 Hrs 95°C	14	15.21 ±0.39**	12673 ± 42	0.82 ±0.021	0.14 ±0.082	0.14 ±0.021	0.55 ±0.065	0.47 ±0.000	88
30	12 Hrs 120°C	100	15.35	12284	0.93 ±0.021	0.11 ±0.078	0.15 ±0.071	0.67 ±0.014	0.52	90
	1.9 Sp. Gr. Float		15.65	12879	1.26	0.84	0.01	0.41	0.82	
33	24 Hrs 102°C	14	13.81 ±0.064	13146 ± 160	0.79 ±0.021	0.15 ±0.000	0.05 ±0.057	0.58 ±0.028	0.25 ±0.031	82
	1.9 Sp. Gr. Float-1.3 Sp. Gr. Sink		22.43	11637	1.46	1.06	0.00	0.40	0.99	
34		14	21.84	11754	0.77	0.21	0.11	0.45	0.31	80

*All experiments were performed with 5% w/w iron reagent containing 4% w/w H_2SO_4

**Standard deviations indicate multiple analyses

the whole 1.3 sink fraction was used in float-sink separation at 3/8-inch top-size with Meyers Process reagent solution followed by size reduction to 14 mesh x 0 and 24 hours leaching at 102°C. Table 11 presents the data. The combined coal, the bypassed 1.3 float (31% of the whole MCM coal) plus the processed sink (69% of the whole coal), met the sulfur-oxide emission standard. Comparison of these data with that in Figure 4, after making proper adjustments for the lower starting pyritic sulfur in the sink (reaction during separation), led to the conclusion that leach solution separated 1.3 sink reacts with a rate constant approximately equal in value to that determined for the whole MCM coal ($K_L = 0.10\ W_p^{-1}$ hr^{-1} at 102°C). This rate constant is approximately 30% higher than expected if it is assumed that the 1.3 float-sink separation did nothing more than increase the value of W_p in the sink by flotation of part of the pyrite-free matrix of the MCM coal. (For the pyrite leaching rate to remain constant the ratio of K_L to pyrite-free coal matrix must remain constant.)

Limited coarse coal processing performed with the mine cleaned gravity fractions demonstrated that size reduction of the 1.9 float-1.3 sink fraction from 3/8-inch to 14 mesh top-size increased K_L by a factor of approximately six; this is to be compared to the factor of 3-4 observed from similar size reduction of the ROM coal and its gravity fractions. None of the processed 3/8-inch top-size coal samples met the NSPS for sulfur-oxides. However, based on the computed K_L value, none of them received sufficient processing (maximum processing time used was 48 hours at 102°C).

TABLE 11. GRAVICHEM PROCESSED MCM COAL (14 x 0 MESH)

Coal	Ash % w/w	Heat Content, Btu/Lb	Total Sulfur, % w/w	Pyritic Sulfur, % w/w	Sulfate Sulfur, % w/w	Organic Sulfur, % w/w	Lbs Sulfur per MM Btu
Leach Solution Float (1.3 sp. gr.)	5.37	14,628	0.71	0.15	0.02	0.54	0.49**
Leach Solution Sink (1.3 sp. gr.)	16.09	12,810	1.37	0.84	0.02	0.52	
Processed Sink (24 hours at 102°C)	15.49	12,907	0.86	0.19	0.23*	0.44	0.67**

*Indicates improper wash

**Combined coal meets NSPS for sulfur of 0.6 lbs sulfur/mm btu

3. PRODUCT SULFUR AND IRON RECOVERY INVESTIGATIONS

Each mole of pyrite oxidized and leached by the Meyers Process yields one mole of iron, 1.2 moles of sulfate sulfur and 0.8 moles of elemental sulfur. These products are generated in the leacher-regenerator unit operations as per Equations (4) and (5) or (6) listed below. They must be removed from the system either as a mixture of iron sulfates and elemental sulfur (Equation 7) or as ferrous sulfate, sulfuric acid, and elemental sulfur (Equation 8).

Leacher

$$FeS_2 + 4.6Fe_2(SO_4)_3 + 4.8H_2O \rightarrow 10.2FeSO_4 + 4.8H_2SO_4 + 0.8S \quad (4)$$

Regenerator

$$9.6FeSO_4 + 4.8H_2SO_4 + 2.4O_2 \rightarrow 4.8Fe_2(SO_4)_3 + 4.8H_2O \quad (5)$$

or

$$9.2FeSO_4 + 4.6H_2SO_4 + 2.3O_2 \rightarrow 4.6Fe_2(SO_4)_3 + 4.6H_2O \quad (6)$$

Process Product Per Mole of Pyrite Leached (Overall Process)

$$FeS_2 + 2.4O_2 \rightarrow 0.6FeSO_4 + 0.2Fe_2(SO_4)_3 + 0.8S \quad (7)$$

$$FeS_2 + 2.3O_2 + 0.2H_2O \rightarrow FeSO_4 + 0.2H_2SO_4 + 0.8S \quad (8)$$

Conceptually the mixture of iron sulfates may be recovered as a mixture of iron oxide and gypsum solids by liming appropriate spent reagent split streams or spent wash water. Sulfuric acid may be removed as pure gypsum by liming spent reagent containing more than 2% w/w acid. Ferrous sulfate may be recovered in pure crystalline form by partial vaporization (condensation) of a spent reagent slip stream. Elemental sulfur may be extracted from coal by organic solvents or by heat (vaporization). Iron oxide, gypsum and elemental sulfur may be safely stored in the environment if there is no industrial demand for their use. Ferrous sulfate can be converted to a mixture of iron oxide and gypsum in the solid phase, if there is no market for it.

The only product recovery technique of those listed above amply demonstrated for applicability to the Meyers Process at the start of this program was elemental sulfur recovery by toluene extraction. Tests performed under this study verified the feasibility of the liming and iron sulfate crystallization options presented above for iron and sulfate recovery. Also, alternate techniques to toluene extraction for elemental sulfur recovery were examined and an acetone-water system was selected as the most cost effective sulfur recovery technique of those tested to date. Because acetone is completely miscible with water it is possible to recover elemental sulfur without the need to predry the coal. Furthermore, because iron sulfate is soluble in acetone-water mixtures the elemental and iron sulfate recovery operations may be integrated into a single scheme. Such a scheme is depicted in Figure 5.

The feasibility of major elements of this scheme was proven at bench-scale (extraction efficiency, acetone-sulfur separation, product sulfur purity, acetone retention on dried coal, liming). A preliminary engineering design of the scheme depicted in Figure 5 is presented in the Process Engineering Section of this report (Section 4). The ensuing subsections summarize the experimental effort on sulfur product recovery.

3.1 ELEMENTAL SULFUR RECOVERY FROM PYRITE LEACHED COALS

Previous studies on the Meyers Process (EPA-600/2-76-143a, May 1976) demonstrated that elemental sulfur recovery from pyrite leached coal is virtually complete by a single stage extraction with toluene providing the coal is azeotropically dewatered in the process. (Water is only slightly soluble in toluene; thus it must be displaced from the coal surface by some other means before toluene can extract the elemental sulfur.) This study was aimed at the identification and testing of alternate sulfur recovery techniques expected to lead to cost reduction. Techniques were sought which either would not require that coal be predried (e.g., use of sulfur solvents miscible with water) or would utilize a cheaper solvent or would utilize heat instead of a solvent. Acetone and methylethylketone (MEK) were identified as the most promising candidate sulfur solvents in the water miscible category;

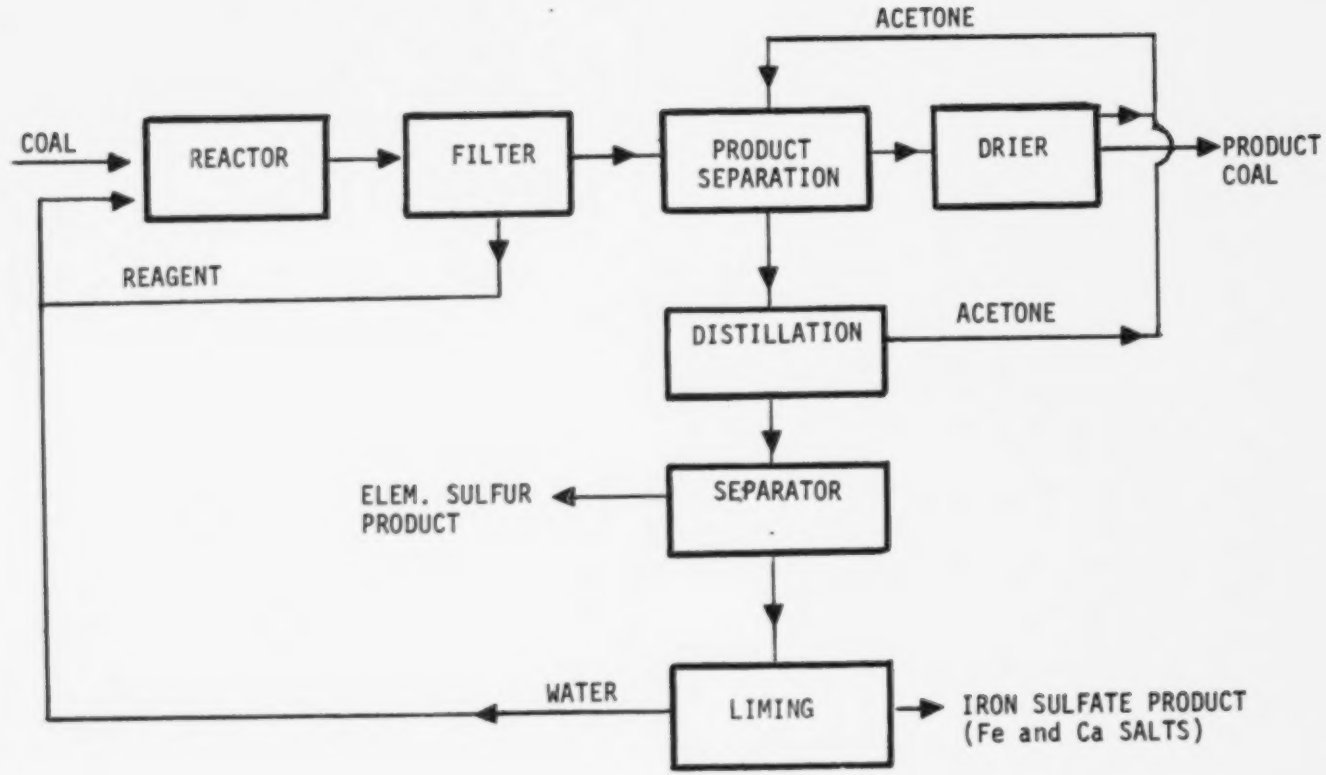


Figure 5. Sulfur and Iron Product Recovery Scheme

hexane, naphtha, or coal derived hydrocarbons were identified as preferable to toluene on the basis of cost and, in the case of the first two, on the basis of product purity (hexane and naphtha being aliphatic hydrocarbons were expected to be more selective solvents of sulfur from coal than toluene); inert gas and vacuum vaporization were examined as potentially promising alternatives to sulfur recovery by solvents.

Feasibility tests on these candidate techniques revealed that acetone is the most desirable alternate to toluene. Acetone is completely miscible with water thus the coal need not be dewatered prior to sulfur extraction. It remains an adequate sulfur solvent even when mixed with appreciable amount of water. It can effect in excess of 90% sulfur recovery in three extraction stages at least one of which is also a coal (reagent) wash stage. Acetone is easily recoverable from coal (less than 0.5% would be retained on the processed coal upon drying on commercial driers based on data generated at TRW and at Wyssmont Co., Inc.* laboratories). It is selective to sulfur (in three stages of sulfur extraction with acetone less than 0.5% of the coal matrix was dissolved).

MEK was also effective in elemental sulfur recovery since it possesses similar properties to acetone. However, it is less miscible with water than acetone and more difficult to separate from dissolved water for recycle (forms azeotropes); also, it is less volatile than acetone and therefore more difficult to recover from the processed coal (at the least it requires higher coal drying temperatures than acetone).

Tests with hexane revealed that up to 80% of the elemental sulfur in processed 14 mesh top-size coal may be recovered in a single extraction stage virtually free of dissolved coal provided the sulfur laden coal was freed of moisture prior to extraction. A second extraction stage recovered less than a quarter of the remaining sulfur on the coal for a total recovery of approximately 85%. Hexane may be used as an alternate to toluene but it is substantially more energy and capital intensive than acetone.

*Commercial drier manufacturer

Elemental sulfur recovery by vaporization into inert gas or vacuum may be feasible in cases where less than 70% recovery is adequate to meet desired sulfur levels in the product coal. Heat treatment of processed coal at ambient pressure under a low flow of inert gas in the 250°-300°C range led to approximately 70% vaporization of elemental sulfur with less than 2% coal volatilization. The same result was obtained with less than 1% coal volatilization at 150°C under vacuum (2 mm Hg pressure). However, temperatures up to 380°C were required for higher sulfur recoveries. At these higher temperatures coal volatilization became appreciable. At 375°C sulfur recovery was complete but approximately 5% of the coal was volatilized together with the sulfur, approximately half of the volatiles were low molecular gases with the remaining being condensable oils and tars. These latter volatiles present processing difficulties which render this approach less desirable than extraction for recovering elemental sulfur from processed coal.

Acetone performance data are summarized in Tables 12 and 13 and in Figure 6. Acetone extractions were performed on leached MCM (mine cleaned Martinka) coal containing between 0.3 and 0.4% by weight elemental sulfur and 20% to 50% moisture. Tests were performed with 14 and 100 mesh top-size coal. Sufficient acetone or acetone-water azeotrope (11% water) was added to the wet coal to produce a 33% solids slurry (based on dry coal weight). Solvent contact time was varied from 0.5 to 2 hours per extraction stage; up to three extraction stages were used. The elemental sulfur content of the coal was determined before and after extraction by two techniques: coal analyses (total sulfur and sulfur forms) and extraction with toluene. The reduction in elemental sulfur indicated by these analyses was balanced against sulfur recovered from the acetone-water solvent.

The data in Table 12 show that the water content of the slurry (water content of the pyrite leached-water wet coal and of the recycled acetone) has a pronounced effect on sulfur recovery in a single stage extraction. In Experiments 1E through 3E the Meyers Process leached coal contained 50% moisture (represents the upper moisture limit of a filter cake) and the acetone used to slurry the coal contained 11% water (represents the water

TABLE 12. ELEMENTAL SULFUR RECOVERY DATA USING AQUEOUS ACETONE EXTRACTIONS

EXP. NO	Feed Coal Moisture % w/w	Water In Feed Acetone % w/w	Acetone In Equilibrated Slurry Liquids % w/w	Contact Time, Hours	Extraction Efficiency* %
1E	50	11	67	0.5	50 ± 8†
2E				1.0	48
3E				2.0	48
4E	20	11	80	2.0	60
5E	20	0	90	2.0	73

*Extraction efficiency represents the percent of input elemental sulfur recovered with a single extraction. The elemental sulfur concentration of the coal used in these extractions was 0.3% w/w.

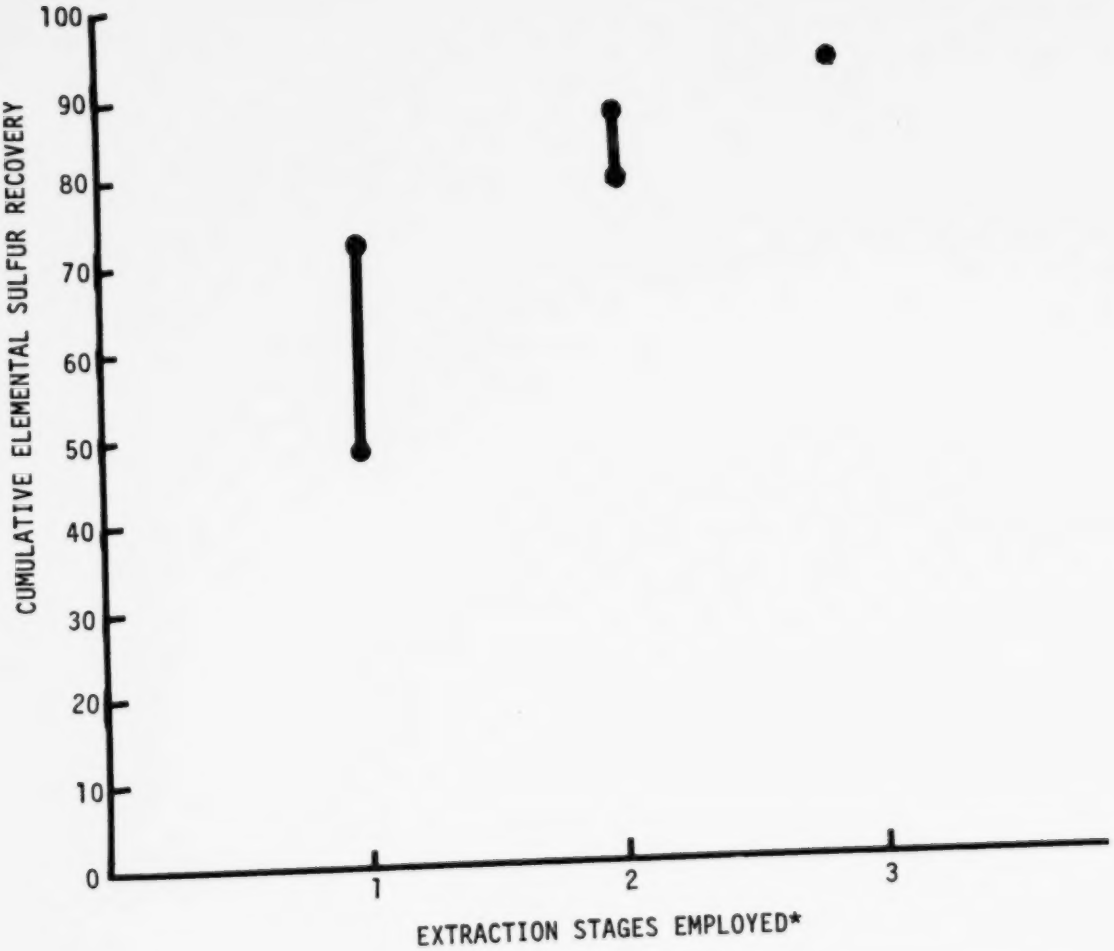
†Two experiments

TABLE 13. MULTI-STAGE ACETONE EXTRACTIONS OF ELEMENTAL SULFUR FROM PROCESSED COAL*

EXP. NO	Coal Top-Size Mesh	Feed Coal Moisture % w/w	1st Stage Extraction Solvent	1st Stage Extraction Sulfur Recovery† %	2nd Stage Extraction Solvent	2nd Stage Extraction Sulfur Recovery† %	3rd Stage Extraction Solvent	3rd Stage Extraction Sulfur Recovery† %	Total Sulfur Recovery† %
6E	14	20	Acetone + 11% H_2O	51	Acetone	29	Acetone	13	93
7E	100	52	Acetone	49	Acetone	32	Toluene	19	100
8E	100	28	Acetone	67	Acetone	17	Toluene	12	96
9E	100	24	Acetone	66	Acetone	21	Toluene	13	100

*One hour extractions of 33% coal slurries at reflux temperatures (56°C for acetone slurries, 110°C for toluene)

†Sulfur recovery is referred to the elemental sulfur content of the processed coal fed to the first stage. The feed coal to these experiments contained 0.4% w/w elemental sulfur.



*These summary date were generated with 14 and 100 mesh top-size coals containing 20-50% moisture and extracted from 0.5 to 2 hours per stage (see Tables 12 and 13 for individual data points).

Figure 6. Elemental Sulfur Recovery by Aqueous-Acetone Mixtures from Meyers Process Leached Coals

content of a 56°C acetone-water azeotrope*). Experiment 5E represents the other extreme where the filter cake contains only 20% moisture and pure acetone is fed to the extraction unit operation. In Experiment 4E the azeotrope was used rather than pure acetone to slurry the 20% moisture coal. The last column in Table 12 shows that extraction efficiency increased from 48% to 73% when the water content in the slurry liquid decreased from 33% to 10%.† However, increase in solvent-coal contact time above 0.5 hours did not affect extraction efficiency (at least in the first stage).

The data in Table 12 indicates that a single stage acetone extraction of wet coal is not adequate for complete recovery of the elemental sulfur product of the Meyers Process. Table 13 presents data which show that three stage, one hour per stage extractions with acetone will extract 93% of the elemental sulfur product on 14 mesh top-size coal without the need to dewater either the feed coal or the feed acetone (Experiment 6E). These data indicate that each stage removed approximately 50% of the elemental sulfur in the coal fed to it. Data from Experiments 7E, 8E and 9E indicate that there is no pronounced effect of coal top-size on elemental sulfur recovery, at least between 14 and 100 mesh top-sizes, and that the water concentration effect observed with 14 mesh top-size coal applies to 100 mesh top-size coals, also. (Note that a slurry prepared from coal containing 52% moisture and pure acetone is equivalent to one prepared from a wet coal cake containing 30% moisture and wet acetone containing 11% water; thus, the water content of the slurries in Experiments 6E and 7E differs by only 20%, 52% vs 42%, therefore the two experiments can be compared for effects of coal top-size). Experiments 7E through 9E represent two-stage acetone extraction studies. The toluene stage was performed to verify coal analysis data which indicated that elemental sulfur recovery was not complete after two-stages of acetone extraction.

---

*The existence of this azeotrope was not verified.

†Nominally 200 grams of leached coal (dry basis) was slurried with acetone or acetone-water mixture to make up 600 grams of total slurry (400 grams total liquid).

Figure 6 summarizes the data and depicts the range of cumulative elemental sulfur recovery attainable in each of the three extraction stages and under all conditions investigated. It is apparent that the largest effect is that of the water content of the slurry. The range of values of percent sulfur recovery narrows as the number of stages increases which, in the case of these experiments, means the water in the system decreases.

In the majority of the experiments performed the acetone-water mixture was separated from the dissolved solids (elemental sulfur and coal matrix) by distillation. The separation was easily accomplished and complete. The distillation residue contained approximately 0.6% w/w of the coal matrix after the first extraction stage and approximately 0.7% w/w at the end of the second and third extractions. Very little coal was dissolved during the second and third stages of extraction. The typical composition of the extracted elemental sulfur from processed MCM coal was 30% sulfur - 70% carbonaceous matter.

3.2 PRODUCT SULFATE AND IRON RECOVERY

Meyers Process chemistry dictates that the pyrite oxidation products of sulfate and iron must be removed at the mole ratio of 1.2. Equations 7 and 8 presented at the beginning of Section 3 show that these two products may be removed conceptually as a mixture of iron sulfates or as a combination of ferrous sulfate and sulfuric acid. Potential removal techniques include the following:

- Evaporation to dryness of spent reagent split streams containing sulfate and iron at 1.2 mole ratio. According to Equation 7 the slip stream must contain 0.6 moles of $FeSO_4$ and 0.2 moles of $Fe_2(SO_4)_3$; that is, the reagent Y value (Fe^{+3}/Fe total ratio) must be 0.4.

- Condensation, partial vaporization, of spent reagent split streams containing sulfur acid to precipitate $FeSO_4$ and partial liming of the supernatant liquid (or a different reagent slip stream) to recover the additional 0.2 moles of sulfate as gypsum.

- Complete liming of spent reagent or spent wash water solutions containing the sulfate and iron species in the proper ratio.
- Combinations of the above techniques.

The technique (or techniques) selected for use in a commercial process will depend on the composition of the reagent used for processing, the Y of spent reagent, the pyrite concentration of the feed coal, and the marketability of the various products. In this study the feasibility of the above options was examined as an aid to the preliminary process design and as a guide to scale-up testing.

Evaporation to dryness of spent reagent was shown to be impractical. When the water content of spent reagent (Y = 0.6 or 0.7) was reduced to approximately 30%, a gel was formed which was difficult to dewater further at ambient pressure. This was partially due to the presence of sulfuric acid in spent reagent and partially due to low melting ferric sulfate hydrates. This technique of recovering the sulfate-iron products is not recommended.

The other three recovery options proved to be feasible and easily accomplished. Pure, crystalline ferrous sulfate hydrates (mono and tetra-hydrates) were recovered from 5% w/w spent iron reagent solution upon evaporation of 50-60% of the water. Liming of acidified iron sulfate reagent solution to yield iron-free calcium sulfate and complete liming of spent reagent and wash water solutions to yield a mixture of iron oxide and gypsum proved readily attainable. Both the evaporation and the liming of solid precipitates dewatered easily (settled readily and filtered rapidly) at lab-scale studies. Lime utilization was estimated at approximately 80%. The solid ferrous sulfate was rapidly and quantitatively converted by solid phase reaction with lime and air to a mixture of iron oxide and gypsum under ambient pressure and near ambient temperature (35°-40°C) conditions; the latter step was investigated as a potential means of disposing ferrous sulfate when nonmarketable.

Table 14 and Figure 7 summarize the parametric influences on ferrous sulfate recovery from spent pyrite leach solutions. Parameters varied were reagent composition (total iron, acid, and Y) and degree of dewatering.

The experiments were performed with approximately 0.8 kg of reagent in stirred 1 liter round bottom glass vessels. The solutions were maintained at their normal boiling points and the evaporated water was continuously condensed and removed from the system until the desired reagent concentration was obtained. Solution normal boiling points varied from 102°C to about 110°C during the concentration procedure. To accurately determine the final saturation concentration of the liquid in the vessel, solution agitation and water removal were discontinued and the precipitated solids were permitted to settle out at the test temperature. A sample of the supernatant liquid was then withdrawn for iron forms analyses. This method eliminated the possibility of redissolving precipitated ferrous sulfate during filtration due to cooling and therby obtaining an erroneously high value for the saturation concentration of ferrous sulfate at the test temperature (solubility of $FeSO_4 \cdot H_2O$ increases with decreasing temperature). Upon filtration the solid crystals were quickly rinsed with water and the filtrate was diluted with distilled water to prevent the precipitation of $FeSO_4 \cdot 7H_2O$ (the solubility of which decreases with decreasing temperature below about 55°C). As a result of these precautions the computed value for ferrous sulfate recovery from before and after reagent analyses (last column Table 14) agreed within 10% with the quantity of precipitate recovered. Analysis of the precipitates revealed that ferrous sulfate was recovered as the monohydrate (the water in the precipitates computed to closer to 2 moles per mole of ferrous sulfate but undoubtedly some tetrahydrate was formed during filtration because of cooling).

Experiments Nos. 1S, 2S, and 3S in Table 14 were performed with 5% w/w iron solutions having a Y value of 0.69 and H_2SO_4 concentrations of 0, 2, and 4% w/w, respectively. Experiment Nos. 4S, 5S, and 6S were performed with nominal 5% w/w iron solutions having a Y value of 0.60 and H_2SO_4 concentrations of 0, 2, and 4% w/w, respectively. Ferrous sulfate was successfully precipitated from each of the six starting reagents. The

TABLE 14. RECOVERY OF FERROUS SULFATE FROM IRON SULFATE H_2SO_4 REAGENT BY EVAPORATIVE CONCENTRATION

Exp. No	Reagent Composition, Wt. % (Except Y Value)								Ferrous Sulfate Recovery* %
	Starting Reagent				Final Reagent				
	Total Fe	Fe^{+2}	H_2SO_4	$(1-Fe^{+2}/Fe)$	Total Fe	Fe^{+2}	H_2SO_4	Y	
1S	4.9	1.6	0.0	0.68	10.4	3.0	0.0	0.71	13
2S	5.0	1.5	2.0	0.69	12.4	3.28	5.2	0.74	22
3S	4.9	1.6	4.0	0.68	12.1	1.69	11.6	0.86	62
4S	5.7	2.3	0.0	0.60	13.5	5.3	0.0	0.61	4
5S	5.0	2.0	2.0	0.60	12.5	2.4	6.6	0.81	63
6S	4.9	2.0	4.0	0.59	12.4	1.6	12.3	0.87	79
Dow†	7.4	4.4	3.5	0.41	11.5	0.92	9.5	0.92	94

*Ferrous sulfate recovery computed from initial and final reagent solution weights and composition and mass balanced against the weight and composition of the recovered precipitate.

†Dow Chemical data presented in EPA Report No. 600/2-75-051.

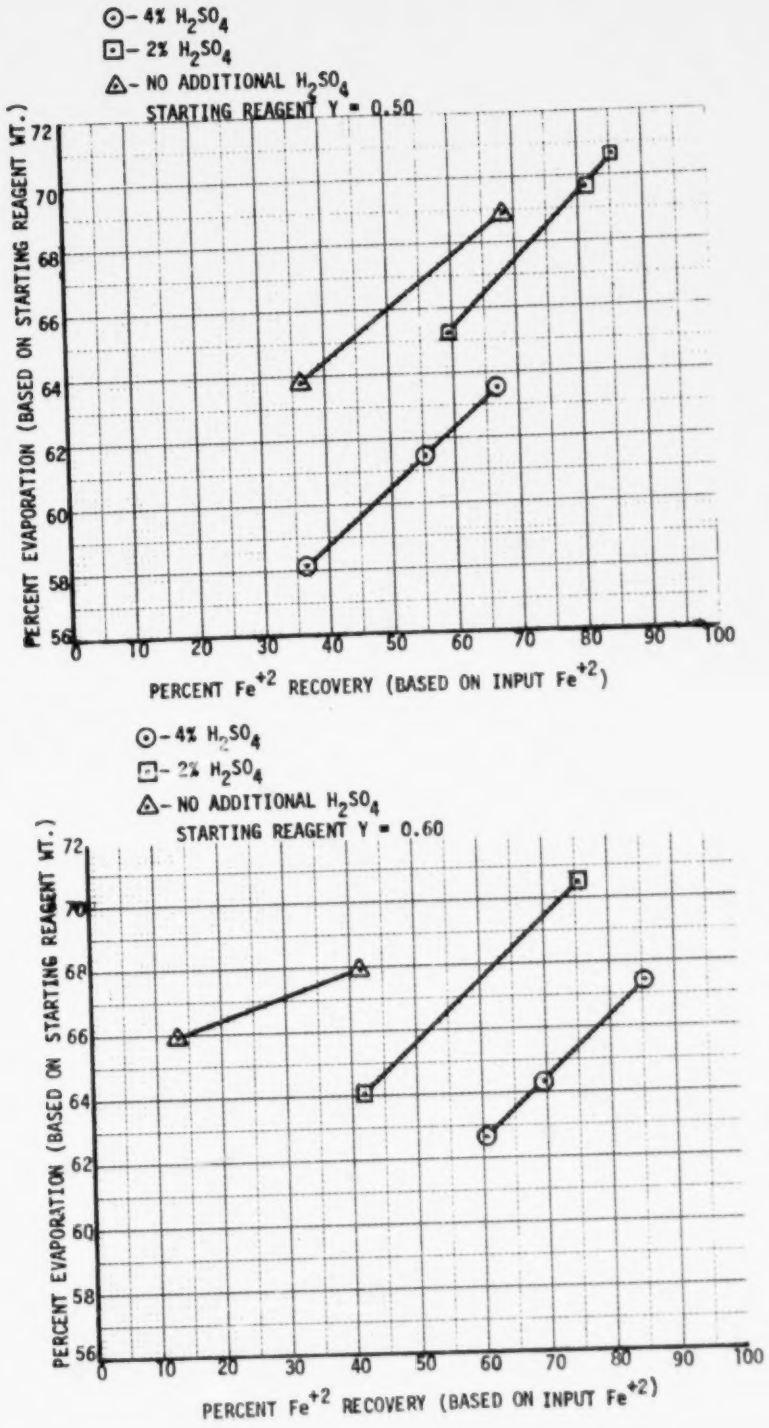


Figure 7. Recovery of Ferrous Sulfate by Evaporative Concentration of 5% w/w Iron Reagent Solutions

extent of ferrous sulfate recovery through precipitation increased with increasing H_2SO_4 concentration (common ion effect) and with decreasing starting reagent Y value. The maximum ferrous iron recovery was attained in Experiment 6S where 79% recovery was achieved and reagent Y was boosted from 0.59 to 0.87. Data from similar experimentation performed by Dow Chemical are presented in the bottom row of Table 14. These further underline the influence of spent reagent Y on quantity and extent of ferrous sulfate recovery.

Figure 7 presents additional data and correlates the effects of Y and sulfuric acid on ferrous sulfate recovery. Evaporated water (as a percent of the quantity of starting solution) is plotted as a function of ferrous iron recovered (as percent of input Fe^{+2}). The data indicate that Fe^{+2} recovery is a linear function of evaporation within the limits of this investigation. Solubility of ferrous sulfate is seen to decrease with increasing acid content and, thus, Fe^{+2} recovery increases with acid content for a given degree of evaporation. Also, the quantity of Fe^{+2} recovered with a specified degree of evaporation increases with decreasing input reagent Y, as expected. However, comparison of data obtained from Y = 0.6 solutions with that from Y = 0.5 solutions shows that this effect diminishes with increasing solution acid content. The 4% w/w H_2SO_4 data for both starting solutions very nearly coincide. Thus, it appears that with initial acid concentrations greater than 4% w/w, ferrous sulfate solubility is low enough that a single straight line plot may effectively express Fe^{+2} recovery as a function degree of evaporation at least in the range of the Y values investigated.

The quoted quantities of precipitates were obtained after one hour at temperature. Experiments were performed where precipitation was allowed to take place in 2, 3, and 24 hours at temperature (the water content was maintained at the desired levels by the use of reflux condensers). There was no difference in the quantity or composition of the precipitates derived from the three reaction times indicating that ferrous sulfate precipitation equilibrates in less than one hour at temperature. The precipitates were readily filterable.

Liming feasibility studies were performed with hot reagent solutions of compositions simulating spent acidified reagent solutions and spent wash water. A typical solution used to simulate spent reagent consisted of 5% w/w Fe, 1.5% w/w Fe^{+2}, and 5.5% w/w H_2SO_4 (4% of the acid represents reagent fed to the leacher and 1.5% represents reagent generated by the oxidation of pyrite). This solution was limed at 70°C with sufficient calcium oxide to remove 73% of the acid. Lime and reagent were contacted for 15 minutes under agitation prior to filtration. The hot filtration yielded virtually pure gypsum solid and solids-free iron sulfate reagent. An iron mass balance showed that at least 96% of the iron remained in solution as expected since the acid was not completely neutralized (0.5 grams of the iron could not be accounted for being in the solution; if it had remained in the gypsum it would have accounted for less than 0.5% w/w iron in gypsum).

In separate studies the above reagent was diluted to stimulate spent wash water which was then completely neutralized with lime. Upon separation of the solids, a mixture of iron oxide and gypsum, the filtrate contained less than one milligram per gram of iron (0.08, 0.02, and 0.00 in three tests) and 1.60-1.70 mg per gram sulfate (theoretical sulfate equilibrium concentration estimated to be 1.5 mg SO_4 per gram of water). In these experiments lime utilization was approximately 80%.

The above feasibility experiments suggested that the appropriate data for the design of liming units for various reagent solution compositions are equilibrium solubility data involving temperature, iron concentration, and acid concentration as parameters. Table 15 summarizes the data generated.

In addition to wet liming of iron sulfate solutions the solid phase reaction of ferrous sulfate with calcium oxide was investigated. This study was based on a paper by Roig et al[1] claiming rapid solid phase

TABLE 15. CALCIUM SOLUBILITY DATA IN IRON SULFATE-SULFURIC ACID SOLUTIONS

Temp °C	Fe Conc. % w/w	Calcium Concentration in Solution (PPM) As a Function of Acid Level (% w/w)					
		C	2	3.2	4	6.4	8
60	5	1284	796		765		
	8	684		574		304	
	10	575			615		458
80	5	1653	1046		545		
	8	996		1228		620	
	10	919			592		287
100	5	1139	985		681		
	8	714		882		466	
	10	574			538		342

liming reaction rates at approximately 20°C and one atmosphere of oxygen. Attempts at TRW to reproduce these data in air (not oxygen) were not successful because of exceedingly slow rates. The rates improved dramatically at approximately 40°C. Ferrous sulfate heptahydrate with a 30% stoichiometric excess of calcium oxide were gradually heated in an oil bath while being mixed. Initiation of the reaction was indicated by a color change from white to light brown at 37°C. The reaction was allowed to proceed for 1 hour at this temperature. Reaction products, free flowing solid granules, were analyzed for ferrous iron content through water extraction of the residual ferrous sulfate. The analysis indicated that at least 99% of ferrous sulfate was converted to iron oxide and gypsum. The data showed that solid hydrated ferrous sulfates precipitated from spent leach solutions by evaporative concentration can be fixated quantitatively through a low temperature solid phase liming operation. The solubility of the iron oxide-gypsum mixture was compared with that of pure gypsum. Samples of the two

solids were placed in water at room temperature for two weeks. The pure gypsum leachate reached its saturation value of 1440 ppm in less than 24 hours; this value remained constant for the remaining two weeks. The iron oxide-gypsum mixture leachate contained 1250 ppm sulfate after 24 hours and reached 1400 ppm only after one week of soaking. Thus, the solid phase reaction product between ferrous sulfate and lime is at least as stable as gypsum in water.

4. PROCESS ENGINEERING

Chemical cleaning of coal, as differentiated from physical cleaning before combustion and from flue gas scrubbing after combustion, is currently at an advanced state of development although none of the several processes is yet commercial. The Meyers Process is clearly among the most advanced, and without question is based on the largest published data base.

Under the previous EPA Contract No. 68-02-1336, a conceptual process design for a commercial scale plant was prepared in mid 1975[2]. It was evident at that time that attractive reduction in process costs could be obtained by separating coal into fractions for processing. Thus, much of the present experimental work was aimed at finding the most desirable approach for separating and processing coal.

As discussed in Section 2 the Martinka mine coal has been separated into both size fractions and specific gravity fractions. Generally it was found that when the coal was ground to slurryable size, all of the size fractions had enough pyritic sulfur to require chemical leaching. Likewise it was found that all size fractions or the combined coal could be separated into two specific gravity fractions, one of which was very low in pyrite. There was no apparent benefit to separation by size in making the equilibrium specific gravity separation. However, commercial coal cleaning plants do not attain equilibrium gravity separation. It is known that commercial coal cleaning facilities using continuous flow equipment cannot economically gravity separate the fines which would require excessively long settling times. The fines, usually that part less than about 100 mesh, are separately handled and may be given some beneficiation in flotation cells.

Although the extent of departure from equilibrium is not truly predictable, it is reasonable to assume that a large fraction of low pyrite Martinka mine coal, probably one-third to one-half, can be gravity separated by a mechanical cleaning facility. Review of published equilibrim gravity separation data for many other coals leads to the general conclusion

that the Martinka coal has typical characteristics. It was decided that the baseline process design would use coal characteristics closely resembling those obtained from Martinka mine whole coal. Reasonable adjustments to the baseline economics could be made to allow for the greater plant throughput that would occur by bypassing a low pyrite fraction. Thus, the Design Basis, the Process Design, and the Energy and Material Balance presented in Sections 4.1, 4.2 and 4.3, respectively, are for this baseline whole coal design case.

At the conclusion of the process engineering effort, and at least partly as an outgrowth of evaluating the results, a dramatically modified approach to the separation step was identified. This approach is based on using the high specific gravity leach solution to first effect the gravity separation and then to remove the pyrite from the pyrite-rich fraction by the conventional Meyers Process. Limited testing showed that the expected equilibrium separation occurs and several non-equilibrium tests tended to show that this process helped to overcome the problem that conventional gravity separation facilities have with cleaning the fines. In this process the fines tended to remain suspended and were withdrawn with the low pyrite, low specific gravity float fraction. Since the fine coal particles contained pyrite which reacted rapidly with leach solution, much of the pyrite in the fines was chemically removed during the mixing and separation step. Even more could have been removed if additional time had been allowed in hot leach solution before the coal was filtered from the solution. It is the potential for gravity separating the full size range of slurryable coal with leach solution to give a lower sulfur "float" product that makes the recent process innovation so attractive. A full process design for this gravity-separated process option was not undertaken during this program, but guidance and preliminary information has been included.

4.1 DESIGN BASIS

There are three general process configurations that are appropriate for chemically cleaning coal based on the Meyers Process. Figure 8 presents in block diagram format the main steps of each configuration. The

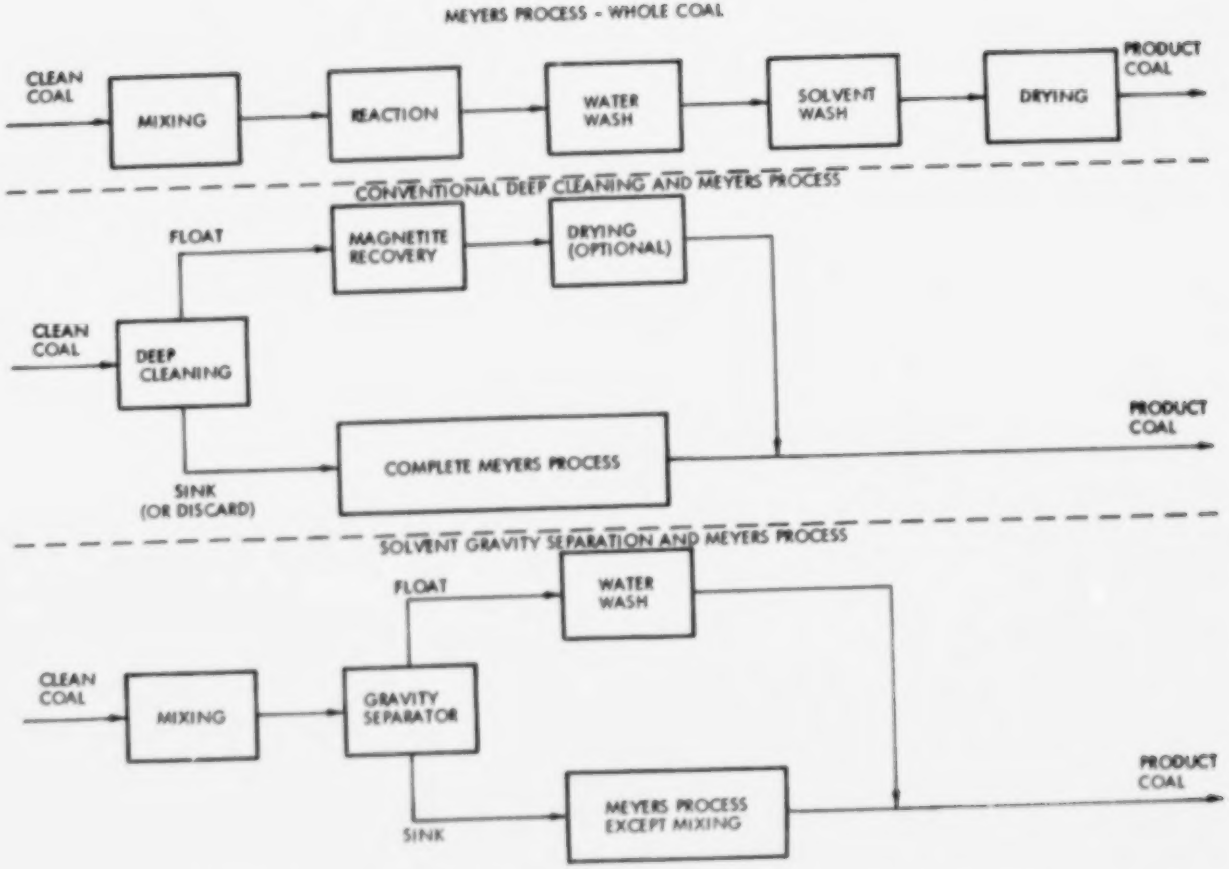


Figure 8. Chemical Cleaning of Coal with the Meyers Process

diagram shows that the main features of the baseline Meyers Process are a key part of each configuration. It is also evident that the two separation options remove "inert coal" containing little pyrite, from "reactive coal" containing pyrite. Thus, in the reactive sink fraction, no new chemistry is present and reaction time is unchanged. However, the reaction volume, the water and solvent washing quantities and drying requirements are all less when only the sink fraction is processed.

The design basis for the whole coal baseline process is drawn from the bench-scale data for suspendable fine coal processing. Suspendable coal is coal of a small enough particle size that it may be processed as a substantially uniform slurry with moderate mixing energy. Although no sharp top-size specification can be given, it appears that coals with top-sizes up to about 8 mesh may be classed as suspendable. Bench-scale experiments were conducted using 14 mesh and 100 mesh top-size coals as representative of the suspendable type. Either of these sizes are often referred to as fine coal.

Processing coal to remove pyritic sulfur using aqueous iron sulfate involves three major process section, each containing several unit operations.

The reactor section which includes mixing and solution regeneration has three main process requirements which are:

- Providing mixing and wetting of ground coal with the aqueous ferric sulfate leach solution and raising the slurry to the operating temperature and pressure.
- Providing the residence time and reaction conditions which remove a nominal 88% of the pyrite originally contained in feed coal.
- Providing the residence time and reaction conditions which regenerate the ferric sulfate solution from the spent iron sulfate leach solution.

The washing section which includes coal washing with acetone and water, several filtration stages, and a centrifugation step has three main process requirements which are:

- Providing for contact of the leach solution-wet coal with a minimum quantity of wash water to remove water soluble iron sulfates.
- Providing for solvent (acetone) contact to remove elemental sulfur from the processed coal.
- Providing for separation of coal from the leach solution, acetone and wash water.

The solvent recovery section which dries the coal product, recovers the acetone from the wash section effluents and removes excess iron sulfate from the process, has four main process requirements which are:

- Providing the thermal environment necessary to reduce the solvent (acetone) level of the coal to the desired level.
- Providing for the recovery of acetone from the wash section effluents by using a stripping column.
- Providing for the recovery of wash water from the wash section effluents by removal (neutralization) of excess iron sulfates.
- Providing for the separation of the byproduct sulfur and neutralization product from the recycle streams.

Specific information and data for the steps or operations which are important to the basic process design are presented in the following paragraphs.

Mixing - The present bench-scale effort confirmed an earlier observation that there is a more critical aspect to the mixing operation than simply surface wetting the particles and suspending them in the leach solution. Preparing the slurry can be readily accomplished with mixing times of a few minutes but it was found that such a slurry will foam when it is pressurized and raised in temperature. Based on laboratory and bench-scale experience, the mixing time for a high rank, high ash, dry coal should be between 30 and 60 minutes at the normal boiling point of

the solution if subsequent foaming is to be avoided. Lesser times may be possible with moist or low rank coal. The quantity of foam produced seems to decrease with increasing coal particle size and to decrease with lower solids content in the slurry. These are secondary parameters which will not be considered of major importance in the process design and for lack of information the influence of slurry depth in the mixer will be ignored.

Leach Reaction - The net overall reaction between pyrite and the ferric sulfate leach solution is represented by:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8\ S \qquad (9)$$

$$\Delta H = -55\ \text{Kcal/g-mole}\ FeS_2 = 0.10\ \text{MM btu/lb-mole}\ FeS_2\ \text{reacted}$$

The reaction rate was found to have a second order dependence on both the fraction of pyrite (or pyritic sulfur) in the coal and the fraction of the total iron in the leach solution which is in the ferric ion form. The leach rate for whole coal at temperatures of interest is represented by the following emperical rate equation:

$$r_L = \frac{-d[W_p]}{dt} = K_L\,[W_p]^2\,[Y]^2 \qquad (10)$$

where $[W_p]$ = wt% pyrite in dry coal at time t,

$[Y]$ = fraction of iron as ferric ion at time t, and

K_L = leach rate constant (a function of temperature and sometimes also W_p).

K_L is independent of total iron concentration at least in the immediate vicinity of 3% to 5% total iron. Physical considerations such as increased solution density and viscosity and the limited solubility of ferrous sulfate in the ferric sulfate solution become increasingly important to the design of the pyrite leacher when the total iron concentration approaches 10%.

The leach rate constant for a whole coal as a function of temperature can be adequately represented by:

$$K_L = A_L \times \exp(-E_L/RT) \qquad (11)$$

where E_L = 11,100 cal/mole,

R = 1.987 cal/mole - °K,

T = temperature in °K, and

A_L = a function of coal top-size.

For 14 mesh top-size coal (mine mouth cleaned Martinka coal) the value of A_L is 2.95×10^5 $(\text{hours})^{-1}(W_p)^{-1}$ for all values of W_p. At the leach solution boiling point (about 102°C), the value of K_L is 0.1 $(\text{hours})^{-1}(W_p)^{-1}$ as calculated from equation (11) (and verified by bench-scale experimentation). Equation (11), along with experimental data, was used to determine the K_L values used in the design of the reactor section. In the baseline design, the mixer operates at 102°C and a K_L value of 0.1 was used as a criteria for design. Likewise, the primary reactor operates at 120°C and the secondary reactor operates at 97°C and K_L values of 0.2 and 0.08 were used respectively. These leach rate constants were considered constant over the range of W_p values for the Martinka coal starting at a W_p of 2.25 and finishing with a value of 0.28 (W_p for product coal).

Regeneration - The leach reaction produces both ferrous sulfate and sulfuric acid which must be processed for continuous recycle operation. For each mole of pyrite reacted 9.6 moles of ferrous sulfate must be regenerated to maintain the acid at a constant level. This gives byproducts for disposal of 0.2 moles of $Fe_2(SO_4)_3$, 0.6 moles of $FeSO_4$ and 0.8 moles of elemental sulfur. Alternately, regeneration of 9.2 moles of ferrous sulfate can be considered if some acid is neutralized to give byproducts of 1.0 mole of $FeSO_4$, 0.2 moles of H_2SO_4 and 0.8 moles of elemental sulfur. The choice of the extent of regeneration should be made on the basis of the byproduct preference and economics within process design constraints. When liming of wash water is used to remove byproducts, the extent of regeneration is not a factor and may be arbitrarily chosen for other reasons.

The regeneration reaction is:

$$1.0\ FeSO_4 + 0.5\ H_2SO_4 + 0.25 \rightarrow 0.5\ Fe_2(SO_4)_3 + 0.5\ H_2O \qquad (12)$$

$$\Delta = -\ 18.6\ \text{Kcal/g-mole}\ FeSO_4 = -\ .0335\ \text{MM btu/lb-mole}\ FeSO_4 \qquad (13)$$

If hydrolysis of a portion of the ferric sulfate to iron oxide should occur as

$$Fe_2(SO_4)_3 + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2SO_4 \qquad (14)$$

then additional acid neutralization or regeneration of ferrous ion would be required to remove the acidity produced from the hydrolysis reaction. The extent of hydrolysis at temperatures below 250°F appears to be small, but at higher temperatures there is some evidence of precipitation of ferric oxide and possibly a low hydrate or anhydrous ferrous sulfate. The hydrolysis products and/or precipitates formed at 265°F were found to redissolve slowly in ambient temperature spent leach solution and do not remain as permanent products. No data was obtained about 265°F.

The regeneration rate was found[2] to be second order in the molar concentration of ferrous ion over the range of ferrous concentration from 100% to less than 1% of the total iron. The rate is:

$$r_R = \frac{-d[Fe^{+2}]}{dt} = K_R\ [Fe^{+2}]^2\ [O_2] \qquad (15)$$

where $[Fe^{+2}]$ = concentration of ferrous ion, mole/liter,

$[O_2]$ = oxygen partial pressure, atm, and

K_R = regeneration rate constant, liters/mole-atm-hour.

Over the temperature range of interest (94°C to 130°C) the rate constant was found to vary exponentially with temperature as

$$K_R = 40.2 \times 10^6 \exp(-13{,}200/RT) \qquad (16)$$

Separation - The major separation step requires treated, fine coal to be separated from the spent leach solution or from solvent which may be wet. The four principal methods which could be employed are hydrocyclones, centrifuges, filters and thickeners. Suspendable coal has a large fraction of particles smaller than 100 microns in diameter and, in general, hydrocyclones are not useful for particle sizes below several hundred microns. Centrifuges and thickness depend on density difference and are not useful for separating coal from the dense leach solution. Filters are the clear choice for this application. For wash water or solvent separations centrifuges can be competitive with filters fitted with solvent control enclosures.

Filtration - The two important design values relating to filtration are the filtration rate and the coal "moisture" content. These values are not independent and are both highly dependent on the specific coal and its properties. For this study, the size and type of filter selected was based on vendor information and on actual pilot scale data obtained in the RTU. The first filter in the wash section separates 14 mesh top-size coal from the spent leach solution. The slurry fed to this filter contains approximately 33% solids. The filter in the RTU unit separates a 14 mesh top-size coal from water (33% slurry) at a measured rate of 250 lbs of coal/ft^2 hr. If this is scaled to the commercial size design basis of 100 tons of coal per hour, a filter area of approximately 800 ft^2 would be required if the coal was being filtered from a water based slurry. Since the first filter in the wash section separates coal from leach solution instead of water, the largest rotary drum filter (Area - 912 ft^2) available was selected to perform this task.

The second and third filters in the wash section separate 14 mesh top-size coal from an organic solution (a mixture of acetone, water and some leach solution). The slurry fed to these filters contains approximately 40% solids, but the specific gravity and the viscosity are less than that of water. The same filtration rate was used to size rotary pan filters with a total area of approximately 900 ft^2 for both the second and third stages of separation in the wash section. Rotary pan filters were selected because they are easily enclosed. Enclosed filters are

necessary at these points in the process to prevent the organic vapors from escaping.

Centrifugation - The size and cost of the centrifuge employed as the final step in the wash section was based primarily on the latest vendor information available. The organic solvent/coal slurry fed to the centrifuge contains approximately 40% solids (14 mesh top-size coal). The centrifuge cake will contain approximately 12% organic moisture after centrifugation. To handle the quantity of slurry fed, two of the largest screen bowl centrifuges currently available were selected. The centrifuges are equipped with dura-metallic seals to contain the organic vapor during centrifugation.

4.2 CONCEPTUAL PROCESS DESIGN FOR COMMERCIAL SCALE

Process engineering studies and trade-offs produced a baseline flow diagram for a commercial scale plant. The flow sheet, which is divided into its three major sections is presented conceptually in Figure 9, drawings 2121-01, -02 and -03. The corresponding mass balance and stream properties are given in Table 16. The baseline plant size was chosen equal to 100 tons of dry feed coal per hour equivalent to about 250 MW power plant feed. This size is about the maximum size for a single train based on available commercial equipment.

Feed and Mixer - Crushed coal, nominally 14 mesh top-size, is fed from feed hopper A-1. The coal is assumed to have 1.2% pyritic sulfur and 10% moisture on a dry basis: thus, the total solids feed rate is 110 tons per hour (TPH) at room temperature, assumed to be 77°F. The coal feed, stream 1, is brought to the mix tank T-1, by conveyor, C-1, and introduced through the rotary feed valve, RV-1. Recycled leach solution, stream 2, at its boiling point (215°F) is introduced to the first mixer stage after first passing through the gas scrubber, SP-1. Steam, stream 3, is needed to raise the feed coal from 77°F to the 215°F mixer temperature. Approximately 5.50 TPH of atmospheric pressure steam is required to heat the coal. This quantity of steam is generated in flash drum, T-4. It is possible that the steam would actually be added to the enclosed

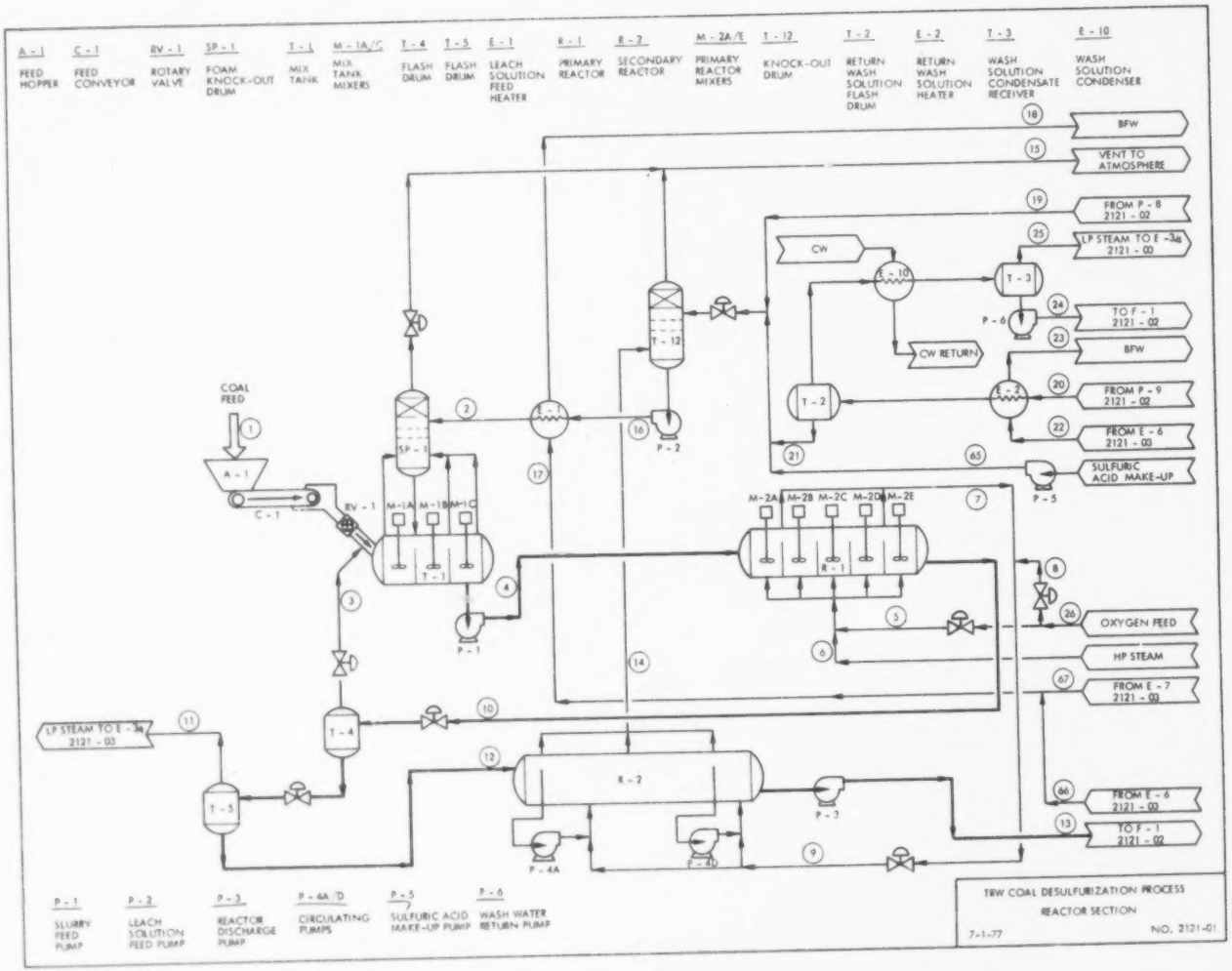

A - 1 FEED HOPPER
C - 1 FEED CONVEYOR
RV - 1 ROTARY VALVE
SP - 1 FOAM KNOCK-OUT DRUM
T - 1 MIX TANK
M - 1A/C MIX TANK MIXERS
T - 4 FLASH DRUM
T - 5 FLASH DRUM
E - 1 LEACH SOLUTION FEED HEATER
R - 1 PRIMARY REACTOR
R - 2 SECONDARY REACTOR
M - 2A/E PRIMARY REACTOR MIXERS
T - 12 KNOCK-OUT DRUM
T - 2 RETURN WASH SOLUTION FLASH DRUM
E - 2 RETURN WASH SOLUTION HEATER
T - 3 WASH SOLUTION CONDENSATE RECEIVER
E - 10 WASH SOLUTION CONDENSER
BFW
VENT TO ATMOSPHERE
FROM P - 8 2121 - 02
LP STEAM TO E -3a 2121 - 03
CW
CW RETURN
TO F - 1 2121 - 02
BFW
FROM P - 9 2121 - 02
FROM E - 6 2121 - 03
SULFURIC ACID MAKE-UP
COAL FEED
OXYGEN FEED
HP STEAM
FROM E - 7 2121 - 03
LP STEAM TO E - 3a 2121 - 03
FROM E - 6 2121 - 03
TO F - 1 2121 - 02
P - 1 SLURRY FEED PUMP
P - 2 LEACH SOLUTION FEED PUMP
P - 3 REACTOR DISCHARGE PUMP
P - 4A/D CIRCULATING PUMPS
P - 5 SULFURIC ACID MAKE-UP PUMP
P - 6 WASH WATER RETURN PUMP
TRW COAL DESULFURIZATION PROCESS
REACTOR SECTION
7-1-77
NO. 2121-01

Figure 9. TRW Coal Desulfurization Process Flow Sheets

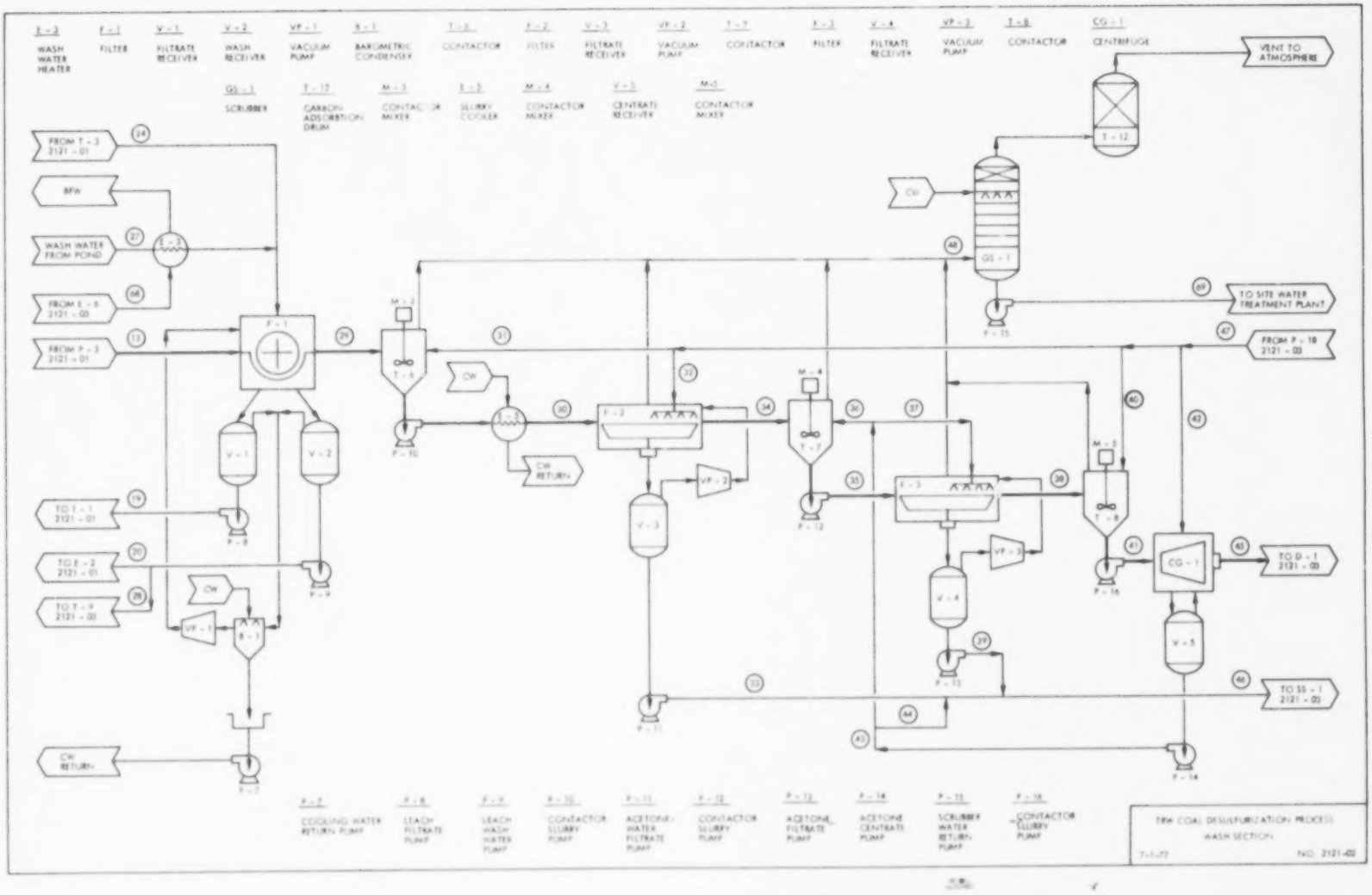


Figure 9. (continued)

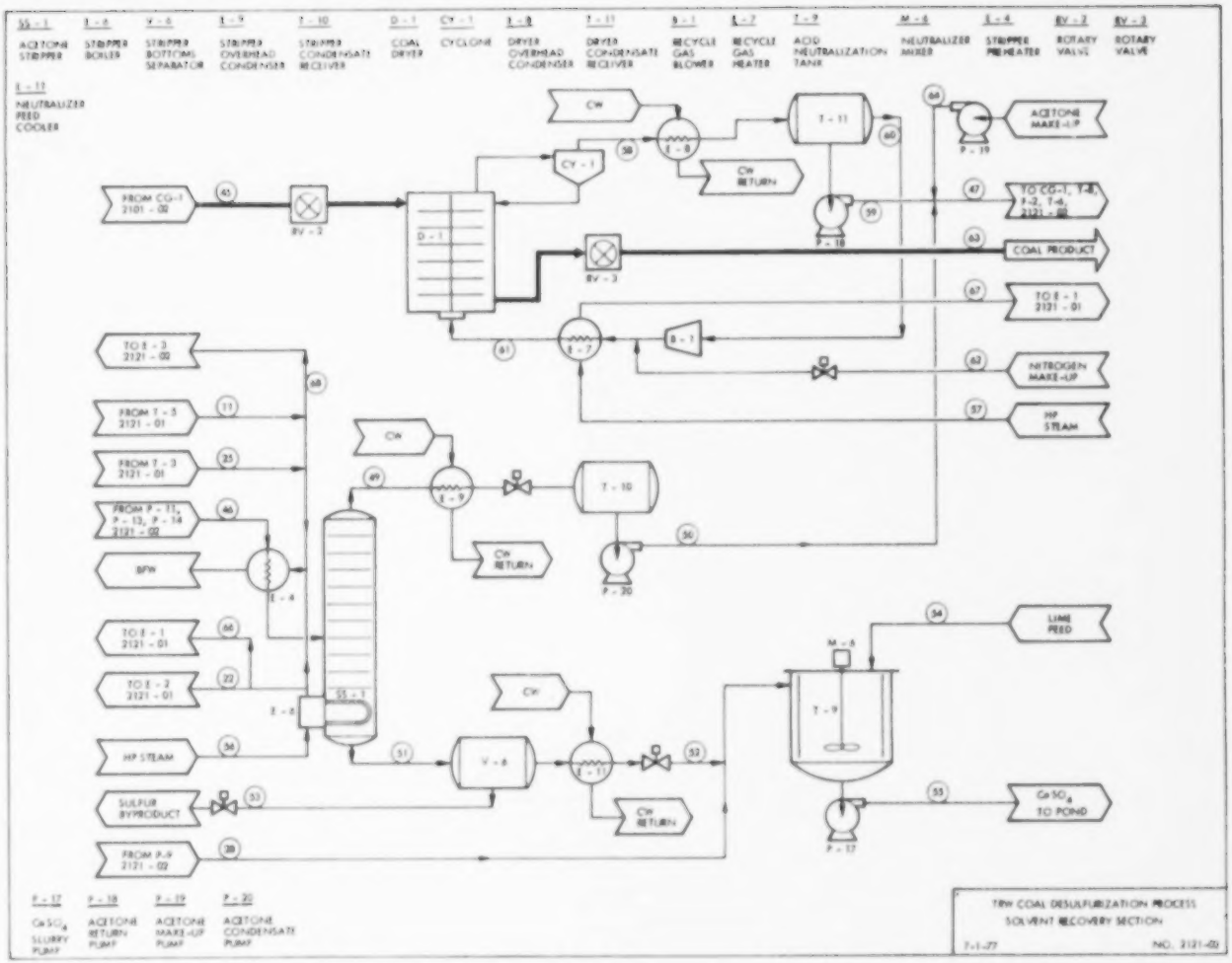

SS - 1 ACETONE STRIPPER
E - 6 STRIPPER BOILER
V - 6 STRIPPER BOTTOMS SEPARATOR
E - 9 STRIPPER OVERHEAD CONDENSER
T - 10 STRIPPER CONDENSATE RECEIVER
D - 1 COAL DRYER
CY - 1 CYCLONE
E - 8 DRYER OVERHEAD CONDENSER
T - 11 DRYER CONDENSATE RECEIVER
B - 1 RECYCLE GAS BLOWER
E - 7 RECYCLE GAS HEATER
T - 9 ACID NEUTRALIZATION TANK
M - 6 NEUTRALIZER MIXER
E - 4 STRIPPER PREHEATER
RV - 2 ROTARY VALVE
RV - 3 ROTARY VALVE
E - 12 NEUTRALIZER FEED COOLER
CW
CW RETURN
FROM CG-1 2101 - 02
ACETONE MAKE-UP
TO CG-1, T-8, P-2, T-6, 2121 - 03
COAL PRODUCT
TO E - 1 2121 - 01
NITROGEN MAKE-UP
HP STEAM
TO E - 3 2121 - 02
FROM T - 3 2121 - 01
FROM T - 3 2121 - 01
FROM P - 11, P - 13, P - 14 2121 - 02
BFW
TO E - 1 2121 - 01
TO E - 2 2121 - 01
HP STEAM
SULFUR BYPRODUCT
FROM P-9 2121 - 02
LIME FEED
$CaSO_4$ TO POND
P - 17 $CaSO_4$ SLURRY PUMP
P - 18 ACETONE RETURN PUMP
P - 19 ACETONE MAKE-UP PUMP
P - 20 ACETONE CONDENSATE PUMP
TRW COAL DESULFURIZATION PROCESS
SOLVENT RECOVERY SECTION
7-1-77
NO. 2121-03

Figure 9. (continued)

TABLE 16. PROCESS MASS BALANCE FOR FINE COAL
(Stream Flows in Tons Per Hour)

	Coal Feed	Feed Soln.	Flash Steam	R-1 Feed	R-1 O_2 Feed	R-1 Steam	R-1 Gas Effluent	R-2 O_2 Makeup	R-2 Gas Feed	R-1 Slurry Effluent	Excess Flash Steam	R-2 Slurry Feed	R-2 Slurry Effluent	R-2 Gas Effluent	Vent O_2	Return Feed Soln.
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Water	10.00	142.01	5.50	157.32		2.25	.06		.06	159.76	3.85	150.41	150.28	.21	.20	142.01
$FeSO_4$		1.34		4.72						1.44		1.44	1.47			1.34
$Fe_2(SO_4)_3$		33.59		29.57						35.98		35.98	36.70			33.59
H_2SO_4		6.97		8.00						6.63		6.63	6.53			6.97
Pyrite	2.25			1.99						0.74		0.74	0.28			
Sulfur				.06						.33		.33	.42			
Coal	97.75			97.75						97.75		97.75	97.75			
Oxygen					1.14		.11	.26	.37					.07	.07	
Inert					.01		.01	Tr	.01					.01	.01	
Total, TPH	110.00	183.91	5.50	299.41	1.15	2.25	.18	.26	.44	302.63	3.85	293.28	293.43	.29	.28	183.91
T, °F	77	215	215	215	77	314	250	77	152	250	215	215	206	206	176	176
P, Psig	0	0	.9	44.5	67.5	67.5	44.5	44.5	25	44.5	0.9	0	15	0	0	5
gpm	-	568	-	952	-	-	-	-	-	955	-	835	917	-	-	583
ρ, lb/ft^3	50.0	80.7	-	78.4	-	-	-	-	-	79.0	-	87.6	79.8	-	-	78.6
Fe, %	-	5.4	-	5.0	-	-	-	-	-	5.2	-	5.4	5.5	-	-	5.4
Y	-	.95	-	.83	-	-	-	-	-	.95	-	.95	.95	-	-	.95
SO_4/Fe	-	1.88	-	2.18	-	-	-	-	-	1.83	-	1.83	1.82	-	-	1.88

(continued)

TABLE 16. (continued)

	LP Steam To E-1	BFW From E-1	F-1 Filtrate Return	F-1 Wash Return	Concentrated Leach Soln.	LP Steam To E-2	BFW From E-2	Wash Water Return	Excess LP Steam	Total Oxygen Feed
	17	18	19	20	21	22	23	24	25	26
Water	30.32	30.32	100.28	57.98	41.72	77.62	77.62	13.10	3.16	
$FeSO_4$			.98	.36	.36					
$Fe_2(SO_4)_3$			24.49	9.10	9.10					
H_2SO_4			4.36	1.62	1.62					
Pyrite										
Sulfur										
Coal										
Oxygen										1.40
Inert										.01
Total, TPH	30.32	30.32	130.11	69.06	52.80	77.62	77.62	13.10	3.16	1.41
T, °F	212	212	160	160	215	212	212	212	212	77
P, Psig	0	0	5	10	5	0	0	10	0	72.5
gpm	-	-	411	236	170	-	-	52	-	-
ρ, lb/ft^3	-	-	79.0	73.1	77.4	-	-	62.3	-	-
Fe, %	-	-	5.5	3.9	5.1	-	-	-	-	-
Y	-	-	.95	.95	.95	-	-	-	-	-
SO_4/Fe	-	-	1.82	1.82	1.82	-	-	-	-	-

(continued)

TABLE 16. (continued)

	Pond Wash Water	Neutra-lizer Feed	F-1 Cake	F-2 Feed Slurry	T-6 Contactor Feed	F-2 Wash	F-2 Filtrate	F-2 Cake	F-3 Feed Slurry	T-7 Contactor Feed
	27	28	29	30	31	32	33	34	35	36
Water	56.90	12.02	50.00	50.00			48.67	1.33	1.36	.03
$FeSO_4$		.07	.05	.05			.05	-	-	
$Fe_2(SO_4)_3$		1.89	1.22	1.22			1.19	.03	.03	
H_2SO_4		.34	.22	.22			0.21	.01	.01	
Pyrite			.28	.28				.28	.28	
Sulfur			.42	.42			.17	.25	.29	.04
Coal			97.75	97.75				97.75	97.75	
Acetone				100.00	100.00	40.00	101.33	38.67	148.64	109.97
Total, TPH	56.90	14.32	149.94	249.94	100.00	40.00	151.62	138.32	248.36	110.04
T, °F	77	160	160	85	85	85	85	85	85	85
P, Psig	30	10	0	15	15	15	15	0	15	15
gpm	228	49	-	1007	505	202	707	-	1057	556
ρ, lb/ft^3	62.3	73.2	-	61.9	49.4	49.4	53.5	-	58.6	49.4

(continued)

TABLE 16. (continued)

	F-3 Wash	F-3 Cake	F-3 Filtrate	T-8 Contactor Feed	Centrifuge Feed Slurry	Centrifuge Wash	Centrate	Centrate To Sulfur Recovery
	37	38	39	40	41	42	43	44
Water	.01	.05	1.32		.05		.05	.01
$FeSO_4$		-			-			
$Fe_2(SO_4)_3$		.03			.03			
H_2SO_4	.01	.01			.01			
Pyrite		.28			.28			
Sulfur	.01	.13	.18		.13		.06	.01
Coal		97.75			97.75			
Acetone	39.99	39.95	148.67	110.00	149.95	40.00	178.18	28.22
Total, TPH	40.01	138.20	150.17	110.00	248.20	40.00	178.29	28.24
T, °F	85	85	85	85	85	85	85	85
P, Psig	15	0	15	15	15	15	15	15
gpm	202	536	756	555	1058	202	900	143
ρ, lb/ft^3	49.4	64.3	49.6	49.4	58.5	49.4	49.4	49.2

(continued)

TABLE 16. (continued)

	Centrifuge Cake	Solvent To Sulfur Recovery	Acetone Return	Filter Vent	Vapor Over-head	Acetone Return	Stripper Bottoms	Stripper Neutral-izer Feed	Sulfur By-Product	Lime Feed	To Pond	HP Steam To E-6	HP Steam To E-7
	45	46	47	48	49	50	51	52	53	54	55	56	57
Water	-	50.00					50.00	50.00			62.13	101.34	12.51
$FeSO_4$	-	.05					.05	.05					
$Fe_2(SO_4)_3$	.03	1.19					1.19	1.19					
H_2SO_4	.01	0.21					0.21	0.21					
Pyrite	.28	-											
Sulfur	.06	0.36					0.36		0.36				
Coal	97.75	-											
Acetone	11.78	278.22	290.00	NIL	278.22	278.22							
Nitrogen	-	-								1.65			
Lime	-	-									5.29		
Gypsum	-	-											
Total, TPH	109.91	303.03	290.00	NIL	278.22	278.22	51.81	51.45	0.36	1.65	67.42	101.34	12.51
T, °F	85	85	85	85	174	85	250	160	250	77	160	417	417
P, Psig	0	15	15	0	15	15	15	10	15	0	5	285	285
gpm	-	1605	1464	-	-	1405	200	200	.80	-	250	-	-
ρ, lb/ft^3	-	51.3	49.4	-	-	49.4	64.4	64.0	112.9	-	67.6	-	-

(continued)

TABLE 16. (continued)

	Dryer Gas Effluent	Acetone Return	Dryer Recycle Gas	Dryer Gas Feed	Nitrogen Makeup	Product Coal	Acetone Makeup	Acid Makeup	HP Hot Water From E-6	HP Hot Water From E-7	LP Steam To E-3	Scrubber Water To Treatment
	58	59	60	61	62	63	64	65	66	67	68	69
Water						-			17.81	12.51	4.16	30.0
$FeSO_4$						-						
$Fe_2(SO_4)_3$						.03						
H_2SO_4						.01		.99				
Pyrite						.28						
Sulfur						.06						
Coal						97.75						
Acetone	77.34	11.68	65.66	65.66		.1	.1					
Nitrogen	68.73		68.73	68.96	.23	.23						
Lime												
Gypsum												
Total, TPH	146.07	11.68	134.39	134.62	.23	98.46	.1	.99	17.81	12.51	4.16	30.0
T, °F	225	85	85	400	77	225	77	77	417	417	212	
P, Psig	5	15	0	10	20	0	15	5	285	285	0	10
gpm	-	59	-	-	-	-	.5	2.17	-	-	-	120
ρ, lb/ft^3	-	49.4	-	-	-	50.0	49.4	113.9	-	-	-	62.4

conveyor to provide heated coal with an effective 15.5% moisture content.

The mixer vessel T-1 was sized for three stages of mixing at 0.25 hours per stage. Under the design guideline that the vessel should be 75% full, the selected mixer size (18' x 36') gives three stages each about 12 feet long and 12.6 feet deep with slightly less than 15,000 gallons in each stage. Any foam generated during coal wetting will be broken down and the entrapped air will be scrubbed in SP-1 by the returning leach solution. The actual air flow through SP-1 is very low and will probably not exceed the air in the bulk coal (50 cubic feet per minute).

Primary Reactor - The fully wetted and deaerated coal slurry from the mixer is pumped by slurry pump P-1 (stream 4) into the first stage of the primary reactor, R-1. Both removal of pyrite and oxidation of ferrous to ferric iron sulfate occur in this reactor. A five-stage reactor was selected since cost studies showed the minimum cost field fabricated vessel had length to diameter ratios near five. The five-stage reactor operating about 85% full would be 22 feet in diameter by 110 feet long operated with pressure capability of about 45 psig including 30 psi of oxygen. The selected vessel size gives five stages each about 22 feet long by 21 feet deep and holding about 57,000 gallons of slurry. At the residence time of one hour per stage, a temperature of 250°F and an oxygen partial pressure of 30 psi, the pyrite is 67% reacted and the leach solution is regenerated to a Y (ferric iron to total iron ratio) of 0.95 in the primary reactor.

Oxygen Loop - Excess oxygen saturated with steam and containing an equilibrium level of inert gas (mainly argon) leaves the primary reactor in stream 7. Makeup oxygen is added to the gaseous effluent from R-1 and fed to the secondary reactor, R-2. The makeup oxygen, stream 8, is added to balance the oxygen used for regeneration in R-2 and that vented to remove inerts. The R-2 gaseous effluent, stream 14, is contacted with returning leach solution in a knock-out drum (T-12) before venting to the atmosphere, stream 15. The vent rate is selected to maintain the inert gas at the design level; namely 10% on a dry basis in R-2.

Assuming 30 psia oxygen pressure, the gas pressures in reactor R-1 at 250°F are as follows:

Oxygen	30.0 psia	
Inert Gas	1.5 psia	
Steam	27.7 psia	
	59.2 psia	(44.5 psig)

Since the feed gas must also overcome the liquid head in the reactor (about 13 psi), the control valve/injector drop (about 10 psi) and other line losses, the gas is fed to R-1 at a total inlet pressure of 82.2 psia (67.5 psig).

The gas pressures in R-2 at 206°F are as follows:

Oxygen	2.3 psia	
Inert Gas	.3 psia	
Steam	12.1 psia	
	14.7 psia	(0 psig)

Since the R-2 feed gas must overcome a 25 psi pressure drop (liquid head plus line losses), it is supplied at an inlet pressure of 39.7 psia (25 psig). The R-1 effluent gas is at 44.5 psig and must be let down to 25 psig before being introduced to the R-2 reactor.

Flash Steam - The heat of reaction and regeneration is dissipated in three ways: temperatures of the oxygen and the feed slurry are raised in R-1, heat is lost from the insulated walls of the mixer and reactors, and water is evaporated from the solutions. Steam is removed by flash drums T-4 and T-5 in dropping the slurry temperature and pressure from reactor R-1 (250°F) to reactor R-2 (206°F). The heat is almost entirely utilized in heating the feed coal and the recycle wash water (in the wash section).

Secondary Reactor - The secondary reactor, R-2, is operated near the atmospheric boiling point with a residence time of 30.5 hours. During this time, additional pyrite is removed from the coal to provide an overall pyrite removal of 88% while the Y of the solution is maintained at 0.95

with an oxygen blanket at a partial pressure of 2.3 psia. This reactor is actually three field fabricated vessels each 26 feet in diameter and 156 feet long. The reactors contain no internal stages, but have circulating pumps to avoid large vertical concentration gradients from occurring in the solution. The slurry from the secondary reactor, stream 13 is pumped by P-3 to the first filter, F-1.

Coal Washing and Sulfur Removal - Bench-scale experience with removal of the sulfate leach solution from coal shows that the solution may be treated as consisting of two types. Surface solution is readily removed by flushing with water or may be readily displaced by a more dilute wash solution. Solution in the pores of the coal particles requires a definite residence time to reach equilibrium with the bulk or surface liquid. The elemental sulfur (formed from the reaction of pyrite with the leach solution) is soluble in acetone and can be removed from the coal cake by contacting with this organic solvent. The coal washing section, therefore, consists of filtration, washing on the filter with water, reslurrying with acetone followed by a second filtration with an acetone wash. The coal cake is contacted with acetone two more times with an intermediate filtration step (and acetone wash). Following the third acetone contracting step, the slurry is centrifuged producing a coal cake containing approximately 12% acetone.

First Filter - Coal slurry from the secondary reactor stream 13, containing about 33% solids is fed to a 12-foot diameter by 24-foot long rotary vacuum filter, F-1. The filtrate from vacuum receiver V-1, stream 19, is pumped, P-8, to the mix tank, T-1, in the reactor section. Clean wash water, streams 24 and 27, is used to wash the filter cake and displace the surface solution on the coal particles. Most of the wash solution, stream 20, is pumped, P-9 to E-2 (located in the reactor section) for excess water removal and then returned to the mix tank in the reactor section. A portion of the wash solution, stream 28, is pumped to the acid neutralization tank, T-9. Vacuum is provided by a 3,000 standard cubic feet per minute (SCFM) vacuum pump, VP-1. The vapors and gases removed from the vacuum receivers, V-1 and V-2, pass through a barometric condenser, B-1,

before entering the vacuum pump. In B-1 most of the flash steam is condensed and enters the cooling water loop where it is pumped to the cooling water tower by P-7.

First Stage Repulping - The washed filter cake from the first filter, stream 29, and fresh acetone are gravity fed through a closed chute to a stirred tank, T-6. This 40,000-gallon tank is operated about three-fourths full to give an average residence time of 30 minutes to equilibrate pore solution with the bulk liquid. This mixed tank may actually be a two-or three-stage tank similar to the mixer (T-1). There would be a minor increase in cost. The slurry, stream 30, is pumped, P-10, to the second stage filter. Any gases introduced with the cake are vented to the scrubbing system, stream 48.

Second Filter - The partially washed slurry, stream 30, containing approximately 40% solids, is cooled to 85°F by heat exchanger, E-5, before second stage filtering. The slurry is filtered and washed with clean acetone, stream 32, in a 24-foot diameter rotary pan filter (two of these filters are required to handle the volume of slurry). Filtrate, stream 33, is pumped, P-11, from the vacuum receiver, V-3, to the acetone stripper, SS-1, in the solvent recovery section. Vacuum for each filter is provided by a 1,500 SCFM vacuum pump, VP-2.

Second Stage Repulping - The wash filter cake with 40% of the elemental sulfur removed and containing only .01% sulfate sulfur, stream 34, is contacted with acetone in two parallel 20,000-gallon stirred tanks, T-7, which may be a single staged vessel similar to the first repulper. The acetone, stream 36, is obtained from the centrate receiver and contains small amounts of water and dissolved sulfur.

Third Filter - The slurry from the second contactor, stream 35, is pumped, P-12, to the third filter, F-3. The slurry is filtered and washed with acetone, stream 37 (obtained from the centrate receiver), in a 24-foot diameter rotary pan filter (again, two of these are required to accommodate the slurry volume). The filtrate, stream 39, is pumped, P-13, from the

vacuum receiver, V-4, to the acetone stripper, SS-1, in the solvent recovery sections. Vacuum for each filter is provided by a 1,500 SCFM vacuum pump, VP-3.

Third Stage Repulping - The washed filter cake with 70% of the elemental sulfur removed, stream 38, is contacted with fresh acetone in stirred tankage, T-8, identical to the second stage repulper. The acetone, stream 40, is obtained from the acetone stripper and the drier in the solvent recovery section.

Centrifugation - The slurry from the third contactor, stream 41, is pumped, P-16, to the centrifuge, CG-1. The slurry with approximately 40% solids is separated in a 44-inch diameter by 132-inch long screen bowl centrifuge (two of these are required) to provide a relatively dry coal cake, stream 45. According to vendor literature and discussions, the coal cake is expected to contain about 12% acetone. The centrate, stream 43, is pumped, P-14, from the centrate receiver, V-5, to provide the wash for the third filter and the feed for the second stage contactor, T-7. That portion (stream 44) of stream 43 which is not required for either F-3 or T-7 is pumped directly to the acetone stripper, SS-1, in the solvent recovery section.

Drying - Coal from the centrifuge, stream 45, is fed to a drier, D-1, through rotary valve, RV-2. In this drier the coal is heated to 225°F by a 400°F nitrogen rich gas stream (actually about 67 volume percent nitrogen and 33 volume percent acetone), stream 61. The fine coal particles are returned to the drier while the gas stream, stream 58, at 225°F is cooled to 85°F in heat exchanger E-8 to condense that quantity of acetone that was removed from the coal in the drier. The liquid acetone is separated from the gas stream in T-11. The recovered acetone, stream 59, is pumped, P-18, back to the wash section. The drier recycle gas, stream 60, containing nitrogen and an equilibrium quantity of acetone is fed by recycle gas blower, B-1, to heat exchanger, E-7, where the gas is heated from 184°F (blower exit temperature) to 400°F with steam (at 417°F and 300 psia). The product coal, stream 63, leaves the drier through rotary valve RV-3 and contains not more than 0.1 percent acetone.

Solvent and Sulfur Recovery - Stream 46 from the wash section containing 84.5% acetone, 15% water, 0.4% salt, and .1% elemental sulfur is heated from 85°F to 106°F by heat exchanger E-4 before being introduced into stripper column, SS-1. The column which operates at 250°F and 15 psig is 13 feet in diameter by 65 feet tall and contains 20 bubble cap trays. The vapor overhead, stream 49, from the column contains essentially all of the acetone that was introduced in the feed, stream 46. The acetone vapor is condensed by heat exchanger, E-9, and collected in stripper condensate receiver, T-10. The recovered acetone, stream 50, is pumped, P-20, back to the wash section after being combined with streams 59 and 64 from the coal drier section. The stripper bottoms, stream 51, contain all the water, salt, and elemental sulfur that came into the stripper in the feed stream. The suspended liquor sulfur is separated from the rest of stream 51 in the stripper bottoms separator, V-6. The liquid sulfur byproduct, stream 53, is withdrawn to storage. The sulfate rich solution, stream 52, is cooled by heat exchanger, E-11, and is sent to acid neutralization.

Neutralization - Sulfate rich wash solution, stream 52, is combined with stream 28 (part of the F-1 wash stream) and fed to a stirred tank T-9. A lime slurry, stream 54, is added to neutralize all of the sulfuric acid and react with all of the salt (the stream is limed all the way to neutrality). Gypsum slurry, stream 55, is withdrawn for disposal and pumped, P-17 to the lime pond. Following the settling out of solids, the water, stream 27, is returned to the wash section as part of the wash water for filter, F-1.

4.3 PROCESS STEAM BALANCE

A flow sheet for the Meyers Process steam balance is shown in Figure 10, drawing 2121-04. High pressure steam is supplied to the process at 417°F and 300 psia. Approximately 4 MM btu/hr, stream 6, of the available steam is used to maintain the temperature of the primary reactor, R-1, at 250°C. About 20 MM btu/hr is supplied, stream 57, to E-7 to heat the recycle drier gas from 184°F to 400°F. The steam condenses in E-7 and leaves, stream 67, as saturated water at 417°F and is combined with stream 66 (high pressure hot water from E-6) to supply heat to E-1, the leach solution feed heater.

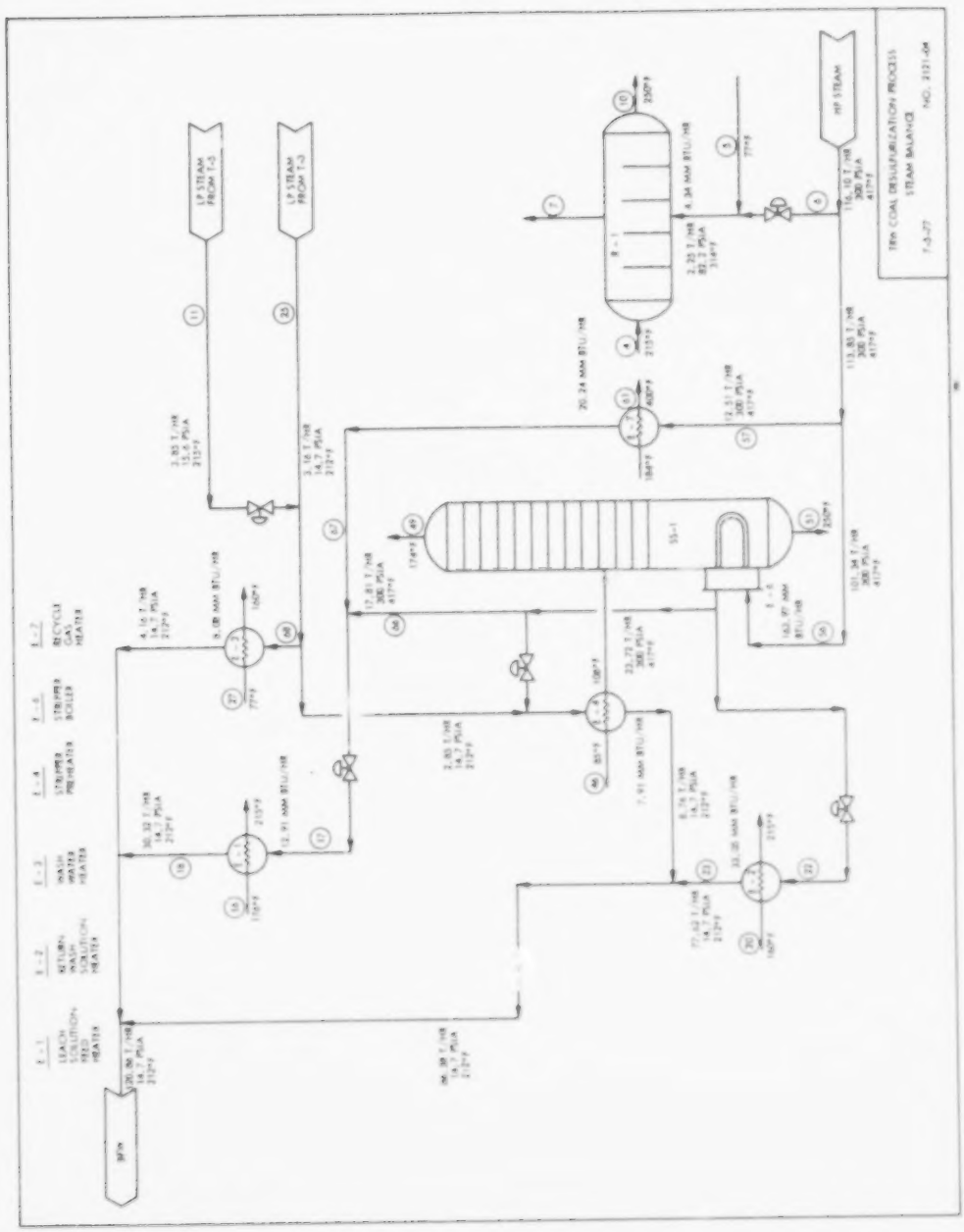


Figure 10. TRW Coal Desulfurization Process Steam Balance

This high pressure water at 417°F and 300 psia is flashed through a valve to produce steam at 212°F and 14.7 psia before it is fed to E-1. The leach solution returning to the mix tank, T-1, is heated from 176°F to 215°F (the mix tank operating temperature) which requires approximately 13 MM btu/hr. The steam condenses in E-1 and exits, stream 18, as boiler feed water (BFW) at 212°F and 14.7 psia.

Most of the supplied high pressure steam (at 417°F and 300 psia) is sent to E-6, which is the reboiler for the acetone stripper column. The column requires approximately 164 MM btu/hr to vaporize the acetone and heat the sulfate/water solution from 106°F to 250°F. The steam is condensed in E-6 and leaves as high pressure hot water at 417°F and 300 psia. The largest part of this hot water is sent to E-2, stream 22, to provide the 33 MM btu/hr required to vaporize the excess water from the leach solution, stream 20, before it is returned to the mix tank, T-1, in the reactor section. The high pressure water is flashed through a valve to produce steam at 212°F and 14.7 psia before it is sent to E-2. The steam condenses in E-2 and exits, stream 23, as boiler feed water at 212°F and 14.7 psia.

A portion of the high pressure hot water from E-6, stream 66, is combined with the hot water from E-7, stream 67, to provide heat to E-1 (as described earlier). A small part of the hot water from E-6 is flashed through a valve to produce low pressure steam and is sent to E-4, the acetone stripper preheater. The preheater heats the acetone and sulfate/water solution stripper feed, stream 46, from 85°F to 106°F which requires approximately 8 MM btu/hr. The rest of the heat required for E-4 is supplied by low pressure steam from flash drum, T-5, and wash solution condensate receiver, T-3, in the reactor section. The low pressure steam condenses in E-4 and is added to the boiler feed water return steam.

The remaining low pressure steam generated in T-3 and T-5 (in the reactor section) is sent to E-3, stream 68. E-3 is the wash water heater which heats the water returning from the settling pond, stream 27, from

77°F to 160°F (requiring about 8 MM btu/hr) before it is used as the wash for filter F-1. The low pressure steam condenses in E-3 and is added to the boiler feed water return stream.

5. PROCESS COST ESTIMATE

Throughout bench-scale development, process costs have frequently been reviewed with an objective of focusing experimental effort in the areas of greatest cost sensitivity. The capital cost of equipment required to perform the pyrite leaching must be carefully controlled to maintain a low processing cost per ton of coal product. A considerable effort has been made to reduce costs in the core processing steps. While some moderate improvements in cost have been made in the basic process compared to the previous design, the major emphasis has centered on obtaining the large cost advantages possible by separating coal into clean and dirty fractions and only processing the dirty fractions. The plan was to obtain maximum benefit from new float/sink technology presently under development at Homer City, Pennsylvania. However, as described in Section 4, an even more exciting approach was discovered using the leach solution to give the separation. The following process cost estimate emphasizes the solution gravity separation economics which are certainly very attractive.

The presentation of the process economics is contained in two sections. Section 5.1 contains the equipment list for a 100 ton per hour (TPH) core process. Section 5.2 contains an estimate capital and operating costs for the two processes involving deep cleaning that were described in Section 4.

5.1 EQUIPMENT LIST

The equipment as shown in Table 17 is divided into the three process sections. For each item the estimated price, FOB factor, is given and an estimate is provided for the installed cost. The items are keyed to the process flow diagram and mass flow rates given in Section 4 and correspond to a single train, core process coal feed rate of about 100 tons per hour equivalent to the requirement of a 250 MW electrical power generation boiler. Capital equipment costs were obtained from various sources: technical literature, equipment suppliers and internal (TRW) costing data. When cost data were obtained from literature or other non-current

TABLE 17. COAL DESULFURIZATION PROCESS EQUIPMENT LIST

REACTOR SECTION		$2.98 MM FOB, $5.86 MM INSTALLED	$K FOB	$K Inst.
1	A-1	Ground Coal Feed Hopper - 5,000 ft^3	$ 16.9	$ 18.7
2	C-1	Feed Conveyor - 20 in. Wide x 20 ft, 5 hp, 200 ft/min	$ 10.1	$ 17.1
3	E-1	Leach Solution Feed Heater - 1,300 ft^2, CS/SS*	$ 31.6	$ 87.3
4	E-2	Return Wash Solution Heater - 2,500 ft^2, CS/SS	$ 54.4	$147.0
5	E-10	Wash Solution Condenser - 420 ft^2, CS/SS	$ 13.4	$ 40.4
6	M-1A/C	Mix Tank Mixers (3) - 15 hp, SS	$ 27.2	$ 44.0
7	M-2A/E	Primary Reactor Mixers (5) - 160 hp, SS	$154.4	$250
8	P-1	Slurry Feed Pump - 1,000 gpm, 70 psi, 50 hp, SS	$ 11.70	$ 32.6
9	P-2	Leach Solution Feed Pump - 600 gpm, 5 psi, 2.5 hp, SS	$ 2.75	$ 7.6
10	P-3	Reactor Discharge Pump - 1000 gpm, 15 psi, 10 hp, SS	$ 5.02	$ 14.0
11	P-4A/D	Circulation Pumps (12) - 1000 gpm, 5 psi, 3.5 hp, SS	$ 40.2	$112
12	P-5	Sulfuric Acid Makeup Pump - 5 gpm, 5 psi, .50 hp, SS	$ 1.17	$ 3.26
13	P-6	Wash Water Return Pump - 50 gpm, 10 psi, .50 hp, CS	$ 1.14	$ 3.78
14	R-1	Primary Reactor - 22 ft ø x 110 ft, Carbon Steel (CS) with SS clad, 45 psig	$724	$1,770
15	R-2	Secondary Reactor (3) - 26 ft ø x 156 ft, SS, 0 psig	$1,610	$2,770
16	RV-1	Rotary Valve - 1 hp, 18 in. x 18 in., 40 RPM	$ 24.8	$ 27.1
17	SP-1	Foam Knock-Out Drum - 3 ft ø x 10 ft, SS, 0 psig, Baffles, Demister Pad	$ 7.0	$ 21.0
18	T-1	Mix Tank - 18 ft ø x 36 ft, SS, 0 psig, 68,500 gal	$120	$210
19	T-2	Return Wash Solution Flash Drum - 1,750 gal, 5' ø x 12', SS, 0 psig	$ 14.72	$ 33.86
20	T-3	Wash Solution Condensate Receiver - 400 gal, 3' ø x 8', SS, 0 psig	$ 9.6	$ 22.1
21	T-4	Flash Drum - 6,100 gal, 7' ø x 21', SS, 0 psig	$ 37.8	$ 86.8
22	T-5	Flash Drum - 6,100 gal, 7' ø x 21', SS, 0 psig	$ 37.8	$ 86.8
23	T-12	Knock-Out Drum - 4,000 gal, 6' ø x 19', SS, 0 psig	$ 26.4	$ 51.5

*CS/SS - Carbon Steel Shell/Stainless Steel Tubes

(continued)

TABLE 17. (continued)

WASH SECTION		$2.45 MM FOB, $4.54 MM INSTALLED	$K FOB	$K Inst.
1	B-1	Barometric Condenser - SS, Condensation Rate = 9.75 ton/hr	As F-1	
2	CG-1	Centrifuge (2) - 44" ø x 132" Screen Bowl Centrifuge, CS, 200 hp	$570	$1,140
3	E-3	Wash Water Heater - 120 ft^2, CS/CS	$ 4.29	$ 13.6
4	F-1	Rotary Drum Vacuum Filter - 12 ft ø x 24 ft, 912 ft^2, SS, 8 hp	$175	$278
5	F-2	Rotary Pan Filter (2) - 24 ft ø, 445 ft^2, SS, 10 hp	$896	$1,420
6	F-3	Rotary Pan Filter (2) - 24 ft ø, 445 ft^2, CS, 10 hp	$527	$1,050
7	GS-1	Scrubber - 5' ø x 30'; 20 trays, 0 psig, CS	$ 11.9	$ 19.5
8	M-3	Contactor Mixer - 50 hp, SS	$ 12.5	$ 20.2
9	M-4	Contactor Mixer - (2) 20 hp, CS	$ 8.0	$ 13.0
10	M-5	Contactor Mixer - (2) 20 hp, CS	$ 8.0	$ 13.0
11	P-7	Cooling Water Return Pump - 1300 gpm, 5 psi, 5 hp, CS	$ 3.0	$ 9.0
12	P-8	Leach Filtrate Pump - 500 gpm, 5 psi, 1.5 hp, SS	As F-1	
13	P-9	Leach Wash Water Pump - 250 gpm, 10 psi, 2 hp, SS	As F-1	
14	P-10	Contactor Slurry Pump - 1000 gpm, 15 psi, 15 hp, SS	$ 5.7	$ 16
15	P-11	Acetone-Water Filtrate Pump - (2) 350 gpm, 7.5 psi, 3 hp, SS	As F-2	
16	P-12	Contactor Slurry Pump - (2) 550 gpm, 7.5 psi, 6.0 hp, CS	$ 3.19	$ 10.5
17	P-13	Acetone Filtrate Pump - (2) 400 gpm, 7.5 psi, 5.0 hp, CS	As F-3	
18	P-14	Acetone Centrate Pump (2) 450 gpm, 7.5 psi, 5 hp, CS	As CG-1	
19	P-15	Scrubber Water Return Pump - 150 gpm, 10 psi, 2 hp, CS	$ 1.41	$ 14.7
20	P-16	Contactor Slurry Pump - (2) 550 gpm, 7.5 psi, 6.0 hp, CS	$ 3.2	$ 10.5

(continued)

TABLE 17. (continued)

			$K FOB	$K Inst.
WASH SECTION				
21	T-6	Contactor - 40,000 gallons, 0 psig, SS	$ 76.8	$176.6
22	T-7	Contactor - (2) 20,000 gallons, 0 psig, CS	$ 32.0	$ 62.7
23	T-8	Contactor - (2) 20,000 gallons, 0 psig, CS	$ 32.0	$ 62.7
24	T-12	Carbon Absorbtion Drum - 5' ø x 10', FRP, 0 psig	$ 2.2	$ 8.6
25	V-1	Filtrate Receiver - 2,000 gallons, Vac, SS	As F-1	
26	V-2	Wash Receiver - 2,500 gallons, Vac, SS	As F-1	
27	V-3	Filtrate Receiver - (2) 1,300 gallons, Vac, SS	As F-2	
28	V-4	Filtrate Receiver - (2) 1,300 gallons, Vac, CS	As F-3	
29	V-5	Centrate Receiver - (2) 1,300 gallons, Vac, CS	As CG-1	
30	VP-1	Vacuum Pump - 3000 SCFM, 200 hp, CS	As F-1	
31	VP-2	Vacuum Pump - (2) 1500 SCFM, 100 hp, CS	As F-2	
32	VP-3	Vacuum Pump - (2) 1500 SCFM, 100 hp, CS	As F-3	
33	E-5	Slurry Cooler - 3,400 ft^2, CS/SS	$ 74.5	$201.6

(continued)

TABLE 17. (continued)

		SOLVENT RECOVERY SECTION $2.46 MM FOB, $3.53 MM INSTALLED	$K FOB	$K Inst.
1	B-1	Recycle Gas Blower (3) CS, 1.7 Compression Ratio; 40 hp	As D-1	
2	CY-1	Cyclone - (3) 5 psig; 850 ft^3, CS	As D-1	
3	D-1	Coal Dryer (3) - 30 ft ø x 55 ft, CS, 5 psig, 15 hp, 54 trays, 60 min residence time	$2,000	$2,500
4	E-6	Stripper Boiler - 940 ft^2, SS	$ 26.8	$ 74.3
5	E-7	Recycle Gas Heater - (3) 85 ft^2, CS	As D-1	
6	E-8	Dryer Overhead Condenser (3) 700 ft^2, CS	As D-1	
7	E-9	Stripper Overhead Condenser - 9,400 ft^2, CS	$108.8	$345
8	E-11	Neutralizer Feed Cooler - 1,300 ft^2, SS	$ 30.0	$ 85.5
9	E-4	Stripper Preheater - 90 ft^2, SS	$ 10.5	$ 46.0
10	M-6	Neutralizer Mixer - 15 hp, SS	$ 6.4	$ 10.3
11	P-17	$CaSO_4$ Slurry Pump - 250 gpm, 2 hp, SS, 5 psi	$ 2.65	$ 7.4
12	P-18	Acetone Return Pump (3) 20 gpm, .50 hp, CS, 15 psi	As D-1	
13	P-19	Acetone Makeup Pump - 1 gpm, .5 hp, CS, 15 psi	$ .77	$ 2.55
14	P-20	Acetone Condensate Pump - 1400 gpm, 15 hp, CS, 15 psi	$ 4.33	$ 14.3
15	RV-2	Rotary Valve (3) - .50 hp, 18 in. x 18 in., 20 RPM	$ 24.0	$ 26.0
16	RV-3	Rotary Valve (3) - .50 hp, 18 in. x 18 in., 20 RPM	$ 24.0	$ 26.0
17	SS-1	Acetone Stripper 13' ø x 65', SS, 20 trays (SS), 15 psig	$182.5	$311.6
18	T-9	Acid Neutralization Tank - 11,000 gal, FRP, 0 psig	$ 6.0	$ 13.8
19	T-10	Stripper Condensate Receiver - 9,500 gal, CS, 15 psig	$ 8.2	$ 16.07
20	T-11	Dryer Condensate Receiver (3) 140 gal, CS, 0 psig	$ 5.2	$ 10.2
21	V-6	Stripper Bottoms Separator - 2,700 gal, SS, 15 psig	$ 17.9	$ 41.2

sources, appropriate cost escalation factors, based on the Marshall and Swift Equipment Cost Index (to escalate costs from date of publication to August 1977), were applied. The FOB equipment cost is the base, uninstalled cost at point of manufacture or point of shipment. The installed equipment cost includes the following elements:

- FOB Equipment Cost
- Field Materials
  - Equipment
  - Piping
  - Concrete
  - Steel
  - Instruments
  - Electrical
  - Insulation
  - Paint
- Material Erection
- Direct Field Labor
- Indirect Costs
  - Freight
  - Taxes
  - Construction Overhead
  - Fringe Benefits
  - Labor Burden
  - Field Supervision
  - Temporary Facilities
  - Construction Equipment
  - Small Tools
  - Miscellaneous Field Costs
  - Contractor Engineering Costs

The installed equipment cost does not include a contingency factor.

5.2 CAPITAL AND OPERATING COSTS

The equipment list presented in the previous section shows that a 100 TPH chemical desulfurization process train has an installed cost estimated to be $13.93 million. Both of the deep cleaning process options described in Section 4 make use of this core desulfurization process to remove the pyrite from the sink fraction. It is convenient for the purposes of discussion and comparison to size the complete coal cleaning plant at 400 TPH which approximates the feed to a 1000 MW power station. Consumables of the process are based on the removal of the equivalent of 1% pyritic sulfur from the 400 TPH of coal feed. It is further assumed that the leach solution separation results in 40% of the coal bypassing the core processing step. This is a conservative choice, since the Martinka results indicate that nearly 50% may be bypassed. In the conventional heavy media separation the design objective 33% bypass was assumed.

The process economic estimates for the leach solution gravity separation are shown in Table 18. These data show that compared to the input coal the price for clean coal energy is increased by 35¢/MM btu for typical utility financing or by about 90¢/MM btu for investor financing.

In evaluating the heavy media float/sink separation, preliminary data for the Homer City, Pennsylvania power generating complex was used. A gravity separation plant costing $32 million and operating at about a 1.3 specific gravity is planned for the feed to three units with a total capacity of nearly 2000 MW. Thus, at 1000 MW the separation plant would cost $15 to $20 million. The complete core desulfurization plant needed would cost about $80 million to give a total of $95 to $100 million. It is unlikely that this approach could be cost competitive with the leach solution separation approach estimated at about $84 million. Clearly emphasis in the future developmental effort should be directed toward the leach solution separation approach.

TABLE 18. LEACH SOLUTION GRAVITY SEPARATION PROCESS ECONOMICS

ENERGY CONTENT OF PRODUCT 82 x 10^6 MM BTU/YR

	RCM Coal Cost		
CAPITAL RELATED REQUIREMENTS, $MM	$15/Ton	$20/Ton	$30/Ton
Battery Limit Capital	39	39	39
Off-Site Capital	16	16	16
Overhead and Profit	12	12	12
Engineering and Design	6	6	6
Contingency	11	11	11
Total Plant Investment*	84	84	84
Interest for Construction	16	16	16
Start-Up Costs	13	17	23
Working Capital (Utility Financing)	13	17	24
Working Capital (Investor Financing)	17	19	28
Total Capital Related Costs (Utility)	126	134	147
Total Capital Related Costs (Investor)	130	136	151
OPERATING COSTS, $MM/YR			
Rat Material (Coal)	48	64	96
Chemicals (Lime, Sulfuric Acid, Acetone)	4	4	4
Supplies	3	3	3
Disposal	1	1	1
Utilities (Including Oxygen)	4	4	4
Labor (48 Positions)	5	5	5
Taxes and Insurance	2	2	2
Total Operating Costs	67	83	115
DESULFURIZATION COST, (Upgrading Cost), $/MM Btu			
Investor Financing, 20% after Tax (DCF)	.86	.90	.95
Utility Financing, Debt/Equity Ratio 75/25 (Return on Debt 9%, on Equity 15%)	.35	.35	.35

*Equivalent to a Plant Capital Investment of $84/KW.

6. GRAVICHEM TREATMENT OF ADDITIONAL COAL SAMPLES

Coal samples were supplied by the Tennessee Valley Authority and Duquesne Power and Light for desulfurization studies. The results are presented in the two sections to follow.

6.1 GRAVICHEM TREATMENT OF TVA COAL

Coal, supplied by TVA from the Cumberland Power Plant at 3/8-inch top-size, was mixed with iron sulfate leach solution (Figure 11), heated to 80°C and allowed to gravity separate in a holding tank to give a 40% yield of float product, after removal of residual iron sulfate leach solution. The float product (Table 19) is a power plant fuel containing 3.1 lbs. $SO_2/10^6$ btu and having a heat content of 14354 btu/lb. The sink fraction (60% by weight) contains most of the coal pyrite.

The sink coal was sized-reduced while still in leach solution to a 14 mesh x 0 coal/leach solution slurry (Table 20), then treated at 102°C according to Meyers Process procedures. The product contained less than 4 lbs $SO_2/10^6$ btu. Thus, both float and processed sink coal met the State Implementation Standard requirements of 4 lbs $SO_2/10^6$ btu.

Thus, there are two products (see photograph in Figure 12) in the gravichem processing of the TVA coal: (1) a gravichem float material of extremely low ash, high heat content and containing about 3 lbs $SO_2/10^6$ btu and (2) a gravichem sink product which is lower in ash and higher in heat content than the input coal, containing nearly 4 lbs $SO_2/10^6$ btu.

6.2 GRAVICHEM TREATMENT OF DUQUESNE COAL

The Duquesne coal from the Warwick mine operating on the Sewickly seam, was supplied from a surge pile at Duquesne's Cheswick Power Plant. The processing conditions were comparable to the TVA coal except that processing was conducted using 1.35 S.G. leach solution (7.5 w/w Fe_2SO_4 and 11% w/w H_2SO_4) for both gravichem and Meyers treatment. 1.35 leach solution was chosen to give a sufficient float fraction based on prior studies. A summary of the data is given in Table 21.

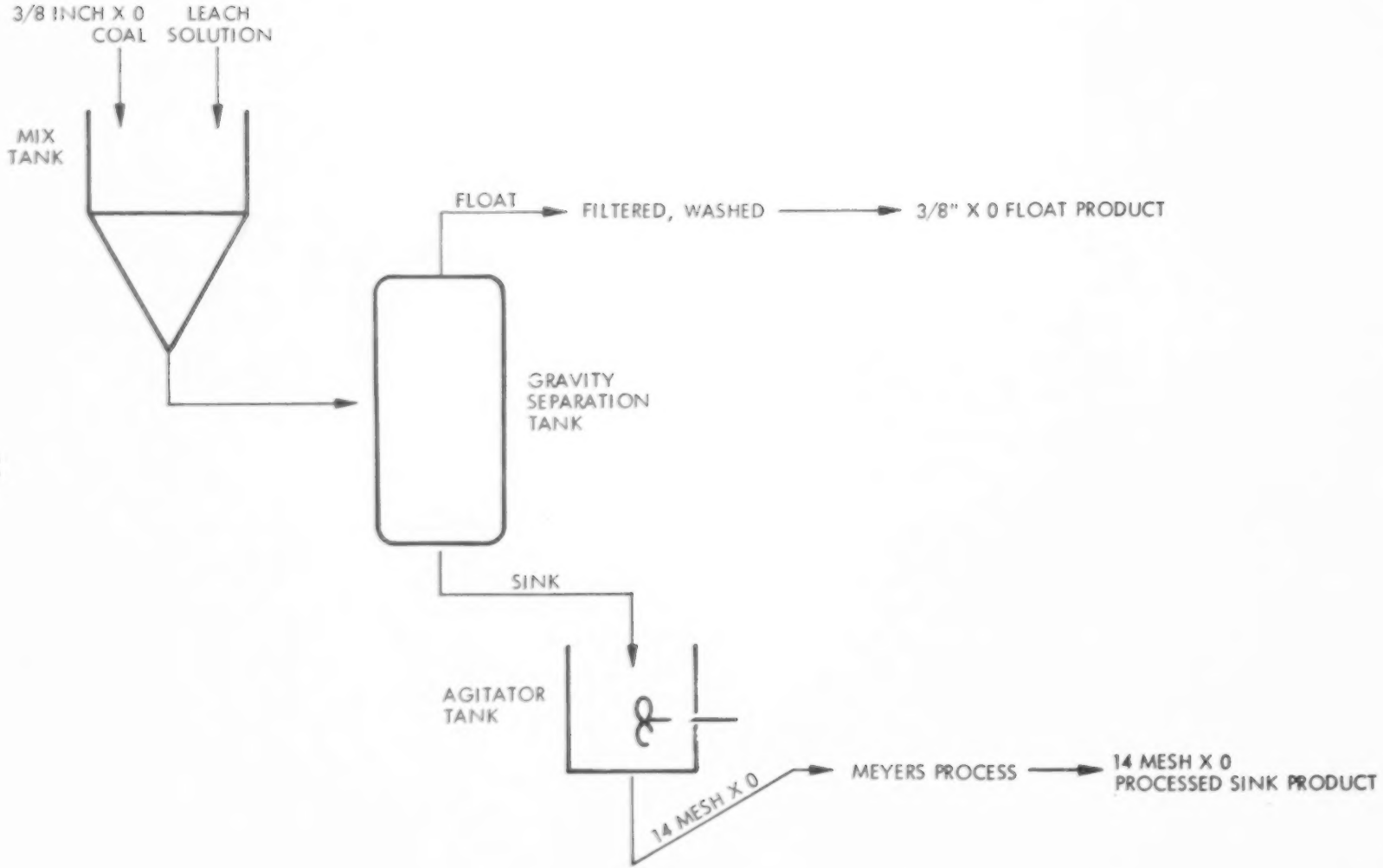


Figure 11. Gravichem Processing of TVA Coal

TABLE 19. GRAVICHEM PROCESSING OF TVA* COAL

Sample†	Analyses: Ash % w/w	Heat Content btu/lb	Sulfur Forms S_T	S_p	S_s	S_o	Fe_2O_3	lbs SO_2/ 10^6 btu
1. As Received	12.79	12414	4.49	1.81	0.48	2.20	2.54	7.24
2. Float (~ 40% w/w of total)†	3.19	14354	2.22	0.39	0.01	1.82	0.56	3.10
3. Sink (~ 60% w/w of total)†	15.15	12295	5.03	2.35	0.00	2.58	6.07	8.18
4. Processed Sink‡	10.31	13000	2.52	0.29	0.40	1.83	0.73	3.87
5. Combined Float and Sink Processed	7.46	13541	2.40	-	-	-	-	3.54

*Kentucky NO. 9 from Cumberland Power Plant, 3/8 top-size.

‡3-hour gravity separation in 1.3 sp. gr. aqueous leach solution [7.5% w/w $Fe_2(SO_4)_3$, 4% w/w H_2SO_4] at 80°C.

†Processed in 1.3 S.G. leach solution (above) for 48 hours at 102°C subsequent to size reduction in Waring blender for 5 minutes @ 15,000 rpm.

TABLE 20. PARTICLE SIZE DISTRIBUTION OF SIZE-REDUCED TVA* SINK COAL

Screen Size	Retained, % w/w
14	1.75
35	3.73
48	9.25
100	23.72
150	14.10
200	12.92
Pan	34.32

*3/8 inch x 0 sink coal in Gravichem leach solution, size-reduced in a Waring Blender for 5 mins at 15,000 rpm.

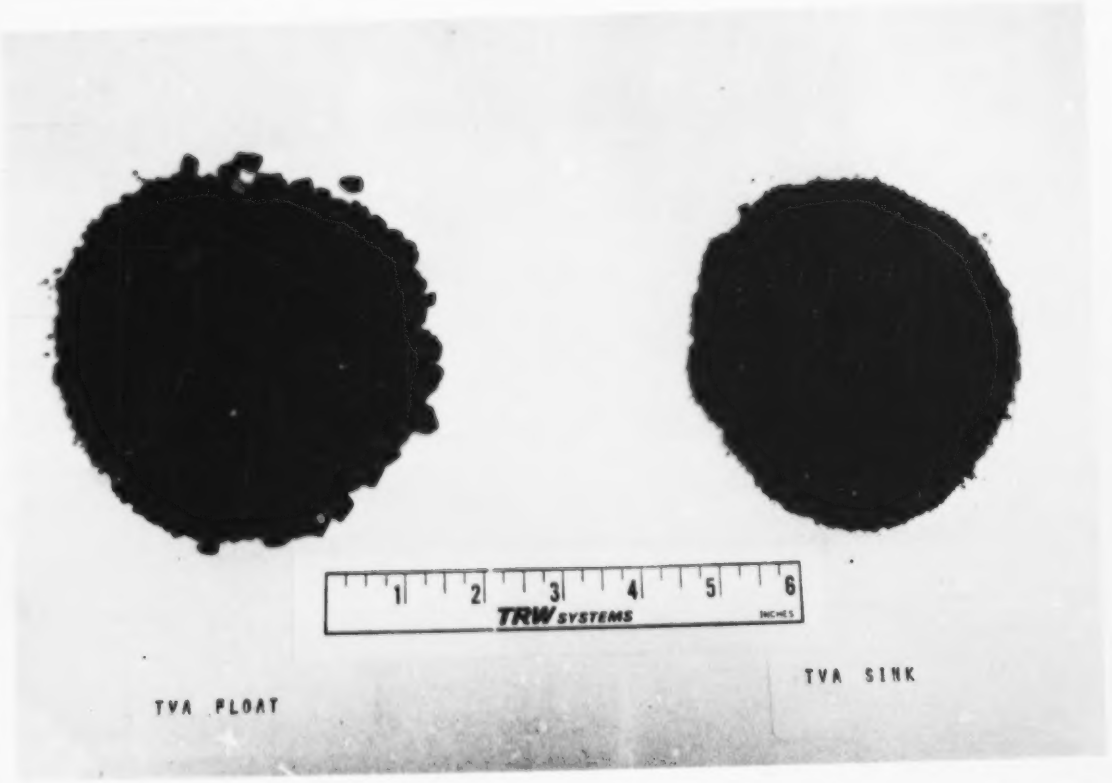


Figure 12. Photograph of Processed TVA Coal

TABLE 21. GRAVICHEM PROCESSING OF DUQUESNE* COAL

Sample†	Analyses: Ash % w/w	Heat Content btu/lb	Sulfur Forms: S_T	S_p	S_s	S_o	Fe_2O_3	lbs SO_2/10^6 btu
1. As Received	17.18	12176	2.13	1.12	0.16	0.86	2.35	3.50
2. Float (~ 50% w/w of total)	6.42	14224	1.46	0.53	0.05	0.88	0.87	2.05
3. Processed Sink‡ (~ 50% w/w of total)	-	11280	1.37	0.36	0.06	0.96	-	2.43

*Cleaned Appalachian coal from Duquesne Light, 1/4" top-size.

†3-hour gravity separation in 1.35 S.G. leach solution [7.5% w/w $Fe_2(SO_4)_3$, 11% w/w H_2SO_4] at 80°C.

‡Processed in 1.35 S.G. leach solution (above) for 48 hours at 102°C, subsequent to size reduction in Waring blender for 5 minutes @ 15,000 rpm.

Although a significant reduction in coal sulfur is evident, it is seen that the Duquesne coal has a high organic sulfur (S_o) content (0.86) which precludes meeting the Federal NSPS, e.g. (1.2 lbs $SO_2/10^6$ btu) even if the pyritic and sulfate sulfur contents were substantially reduced. However, gravichem processing at 14 mesh top-size, rather than 1/4-inch size utilized would have given substantially reduced pyrite in the float coal due to both better pyrite physical release and more pyrite leaching from the coal.

REFERENCES

1. Roig, E., J. F. Hazel and W. M. McNabb. Low-Temperature Oxidation of Solid Ferrous Sulfate Heptahydrate with Oxygen in the Presence of Solid Calcium Hydroxide. J. Am. Chem. Soc., 80:1874-1876, 1958.

2. Koutsoukos, E. P., et al. Meyers Process Development for Chemical Desulfurization of Coal. EPA-600/2-76-143a, U.S. Environmental Protection Agency, Volume I. 1976.

MEYERS PROCESS BIBLIOGRAPHY

1. Lorenzi, L. Jr., J. S. Land, L. J. Van Nice, E. P. Koutsoukos, and R. A. Meyers. Coal Age, 77(11):76, 1972.

2. Meyers, R. A. Desulfurization of Coal. Paper presented at the Symposium on Desulfurization of Coal, 71st National Meeting of the American Institute of Chemical Engineers, Dallas, Texas, 1972.

3. Meyers, R. A. Removal of Pollutants from Coal. Paper presented at the Symposium on Coal Conversion and Environment, American Geophysical Union, Washington, D.C., 1972.

4. Hamersma, J. W., M. L. Kraft, E. P. Koutsoukos, and R. A. Meyers. Chemical Removal of Pyritic Sulfur from Coal. Preprints Div. of Fuel Chemistry, Am. Chem. Soc., 17(2):16, 1972.

5. Lorenzi, L. Jr., J. S. Land, L. J. Van Nice, and R. A. Meyers. Engineering, Economic and Pollution Control Assessment of the Meyers Process for Removal of Pyritic Sulfur from Coal. Preprints Div. of Fuel Chemistry, Am. Chem. Soc., 17(2):16, 1972.

6. Meyers, R. A., J. W. Hamersma, J. S. Land, and M. L. Kraft. Desulfurization of Coal. Science, 177:1187-1188, 1972.

7. Hamersma, J. W., E. P. Koutsoukos, M. L. Kraft, R. A. Meyers, G. J. Ogle, and L. J. Van Nice (TRW Inc.). Chemical Desulfurization of Coal: Report of Bench-Scale Developments, Volumes 1 and 2. EPA-R2-73-173a, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1973.

8. Meyers, R. A. Removal of Pyritic Sulfur from Coal Using Solutions Containing Ferric Ions. U.S. Patent 3768988. 1973.

9. Nekervis, W. F. (Dow Chemical Corp.). The Desulfurization of Coal. Paper presented at the Annual Am. Chem. Soc. Fall Scientific Meeting, Midland, Michigan, 1973.

10. Sinke, G. C. (Dow Chemical Corp.). The Desulfurization of Coal. Paper presented at the 30th Annual Am. Chem. Soc. Fall Scientiffc Meeting, Midland, Michigan, 1973.

11. Hensley, F. F. (Dow Chemical Corp.). Pyritic Sulfur Removal from Coal. Paper presented at the 30th Annual Am. Chem. Soc. Fall Scientific Meeting, Midland, Michigan, 1973.

12. Lorenzi, L. Jr., L. J. Van Nice, and R. A. Meyers. Preliminary Commerical Scale Process Engineering and Pollution Control Assessment of the Meyers Process for Removal of Pyritic Sulfur from Coal. Iron-making Proceedings, AIME, 32:110, 1973.

13. Hamersma, J. W., M. L. Kraft, E. P. Koutsoukos, and R. A. Meyers. Chemical Removal of Pyritic Sulfur from Coal. Advances in Chemistry, Series No. 127, American Chemical Society, Washington, D.C., 1973.

14. Weant, G. E., F. O. Mixon, and F. L. Bellegia (Research Triangle Institute). An Evaluation of Coal Beneficiation by the Meyers Process. Paper prepared under Contract No. 28-02-1325-3 for the U.S. Environmental Protection Agency, Cincinnati, Ohio, 1974.

15. Hamersma, J. W., M. L. Kraft, W. P. Kendrick, and R. A. Meyers. Chemical Desulfurization of Coal to Meet Air Pollution Control Standards. Preprints Div. of Fuel Chemistry, Am. Chem. Soc., 19(2):33, 1974.

16. Lorenzi, L. Jr., L. J. Van Nice, M. J. Santy, and R. A. Meyers. Plant Design of a Method for Chemical Desulfurization of Coal. Preprints Div. of Fuel Chemistry, Am. Chem. Soc., 19(2):43, 1974.

17. Koutsoukos E. P., R. A. Orsini, G. J. Ogle, and R. A. Meyers. Chemical Desulfurization of Coal by the Meyers Process, 73rd National Meeting of the American Institute of Chemical Engineers, Salt Lake City, Utah, 1974.

18. Weant, G. E., F. O. Mixon, and F. L. Bellegia (Research Triangle Institute). An Evaluation of Coal Beneficiation by the Meyers Process. Final Report RTI No. 43U-893-30, Contract No. 68-02-1325-3 for the U.S. Environmental Protection Agency, Research Triangle Park, No. Carolina, 1974.

19. Shepherd, B. P., H. K. Michael, J. S. Wilson (Dow Chemical Corp.). Cost Analysis of Meyers Coal Desulfurization Process. Prepared for the U.S. Environmental Protection Agency, Office of Research and Development under Contract No. 68-02-1329, Washington, D.C., 1974.

20. Hamersma, J. W., et al (TRW Inc.). Applicability of the Meyers Process for Chemical Desulfurization of Coal: Initial Survey of Fifteen Coals. Report No. EPA-650/2-74-025, Contract No. 68-02-0647 for the U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., 1974.

21. Hamersma, J. W., M. L. Kraft, W. P. Kendrick, and R. A. Meyers. Meyers Process Cuts Out 80% Sulfur. Coal Mining and Processing, 11(8):36, 1974.

22. Meyers, R. A., J. W. Hamersma, R. W. Baldwin, J. G. Handwerk, J. H. Gary, and J. O. Golden. Low-sulfur Coal Obtained by Chemical Desulfurization Followed by Liquefaction. Preprints Div. of Fuel Chemistry, Am. Chem. Soc., 20(1):234, 1975.

23. Meyers, R. A. Desulfurization of Coal. Paper presented at the Chemical Engineers Tyler Conference on Sulfur Reduction in Coal, Pittsburgh, Pa., 1975.

BIBLIOGRAPHY (continued)

24. Meyers, R. A. Applicability, Engineering Design and Cost Estimates of a Process for Desulfurization of Coal with Ferric Sulfate. Paper presented at the Symposium on Desulfurization of Solid Fuels, 80th National Meeting of the American Institute of Chemical Engineers, Boston, Mass, 1975.

25. Meyers, R. A., and L. Lorenzi, Jr. Chemical Desulfurization of Coal. In: Hydrocarbon Processing No. 93, 1975.

26. Tek, M. Rasin (Univ. of Michigan). Coal Beneficiation. In NTIS Publication, Evaluation of Coal Conversion Processes to Provide Clean Fuels, Part 2. 1974.

27. Hamersma, J. W., and M. L. Kraft (TRW Inc.). Applicability of the Meyers Process for Chemical Desulfurization of Coal: Survey of Thirty-five Coals. Environmental Protection Technology Series, EPA-650/2-74-025-a, 1975.

28. Nekervis, W. F., and E. F. Hensley (Dow Chemical Corp.). Conceptual Design of a Commercial Scale Plant for Chemical Desulfurization of Coal. Environmental Protection Technology Series, EPA-600/2-75-051, 1975.

29. McGee, E. M. (Exxon Research and Engineering Co.). Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Coal Treatment: Section 1, Meyers Process. Environmental Protection Series, EPA-650/2-74-009-K, 1975.

30. Koutsoukos, E. P., M. L. Kraft, et al (TRW Inc.). Final Report Program for Bench-Scale Development of Processes for the Chemical Extraction of Sulfur from Coal. Environmental Protection Agency Series, EPA-600/2-76-143a, 1976.

31. Van Nice, L. J., and M. J. Santy (TRW Inc.). Pilot Plant Design for Chemical Desulfurization of Coal. Environmental Protection Technology Series, EPA-600/2-77-080, 1977.

32. Van Nice, L. J., E. P. Koutsoukos, R. A. Orsini, and R. A. Meyers. A Process Development Plant for Testing of the Meyers Process. Preprints Am. Chem. Soc. Div. of Fuel Chemistry, 22(2):84, 1977.

33. Hamersma, J. W., M. L. Kraft, and R. A. Meyers. Applicability of the Meyers Process for Desulfurization of U.S. Coal. Preprints Am. Chem. Soc. Div. of Fuel Chemistry, 22(2):73, 1977.

34. Van Nice, L. J., M. J. Santy, E. P. Koutsoukos, R. A. Orsini and R. A. Meyers. Coal Desulfurization of Test Plant Status. 4th Annual International Conference on Coal Gasification, Liquefaction and Conversion to Electricity, Univ. of Pittsburgh, Pa 1977.

BIBLIOGRAPHY (continued)

35. Meyers, R. A. Chemical Desulfurization of Coal. In Dispersion and Control of Atmospheric Emissions, New-Energy-Source Pollution Potential, AIChE Symposium Series No. 165, 1977, pp 179-182.